PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-228692
(43)Date of publication of application : 24.08.1999

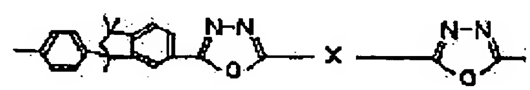
(51)Int.Cl. C08G 73/08
C09K 11/06
H05B 33/14
H05B 33/22

(21)Application number : 10-028607
(22)Date of filing : 10.02.1998

(71)Applicant : JSR CORP
(72)Inventor : PATZ MATTHIAS
TAKAHASHI MASAYUKI
GOTO KOHEI

(54) POLYOXADIAZOLE DERIVATIVE, ITS PRODUCTION AND ORGANIC ELECTROLUMINESCENT ELEMENT

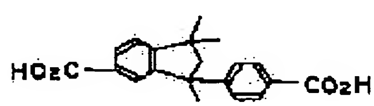
(57)Abstract:
PROBLEM TO BE SOLVED: To obtain the subject polymer soluble in an organic solvent, capable of exhibiting excellent heat stability and electron transporting properties, useful as an organic electroluminescent element, etc., by introducing a phenyl indane group-containing oxadiazole segment into a molecule.
SOLUTION: This polyoxadiazole derivative comprises a segment of formula I (X is a group of the formula Ar-(Z-Ar)n {Ar is a bifunctional (heterocyclic) aromatic group; Z is a group of the formula CRR [R is H, a 1-6C (halogenated) alkyl or a 6-30C aryl], a group of the formula CR=CR, O, S or SO2; (n) is 0-2}) and is obtained, for example, by reacting a compound of formula II with a 1,1,3-trimethyl-3-phenylindane-4',5-dicarboxylic acid of formula III.



I

$$H_2NHNOC-Ar-\left(Z-Ar\right)_n-CONHNH_2$$

II



III

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

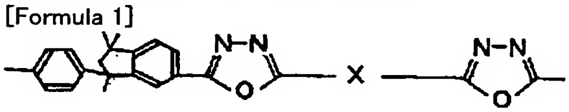
[Date of registration]

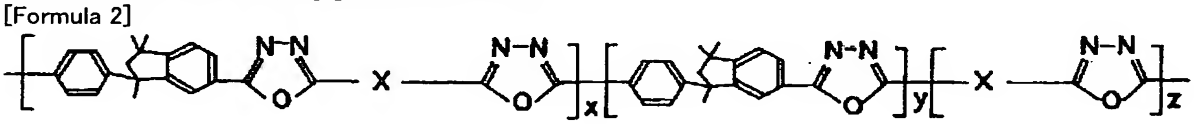
[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

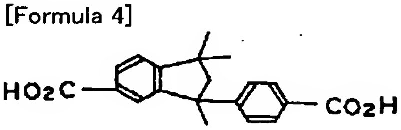
CLAIMS

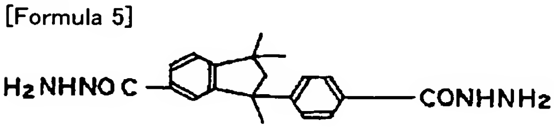
[Claim(s)]
[Claim 1] The polyoxadiazole derivative characterized by containing the segment expressed with the following general formula (1) to intramolecular.
[Formula 1]

(1)

X is expressed with -Ar-(Z-Ar) n- among [type (1), and Ar shows a divalent aromatic series radical or a divalent heterocycle type aromatic series radical among the X concerned. Z - CRR- or -CR=CR - (R expresses hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, or the aryl group of carbon numbers 6-30.) the hydrocarbon group expressed, and O, S and SO2 It is at least one and n is the integer of 0, or 1-2.]
[Claim 2] The polyoxadiazole derivative characterized by the polyoxadiazole derivative which contains the segment expressed with said general formula (1) in a polyoxadiazole derivative according to claim 1 being the compound expressed with the following general formula (2).
[Formula 2]

(2)

Among [general formula (2), Ar, Z, and n are the same as that of the contents of the general formula (1) respectively, the mole ratio of x:y is the value of 100:0-100:1000 within the limits, and the mole ratio of x:z is the value of 100:0-100:500 within the limits.]
[Claim 3] the logarithm of said polyoxadiazole derivative — the polyoxadiazole derivative according to claim 1 or 2 characterized by making viscosity etainh (Measuring condition: the temperature of 30 degrees C, a solvent sulfuric acid, concentration of 0.5g / dl) into the value of 0.1 - 2 dl/g within the limits.
[Claim 4] 1 expressed in the following formula (4) as the aromatic series dicarboxylic acid dihydrazide expressed with the following general formula (3), 1, 3-trimethyl-3-phenyl indan - 4', the manufacture approach of the polyoxadiazole derivative characterized by making 5-dicarboxylic acid react.
[Formula 3]

$$H_2NHNOC-Ar\left(Z-Ar\right)_n CONHNH_2 \qquad (3)$$

[Formula 4]

(4)

Ar shows a divalent aromatic series radical or a divalent heterocycle type aromatic series radical among [general formula (3), Z is the hydrocarbon group expressed with -CRR- or -CR=CR- (R expresses hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, or the aryl group of carbon numbers 6-30.), and at least one of O, S, and the SO2, and n is the integer of 0, or 1-2.]
[Claim 5] 1 expressed with the following type (5), 1, 3-trimethyl-3-phenyl indan - The manufacture approach of the polyoxadiazole derivative according to claim 4 characterized by making it react including further 4', the aromatic series dicarboxylic acid expressed with 5-dicarboxylic acid dihydrazide and the following general formula (6), or either.
[Formula 5]

(5)

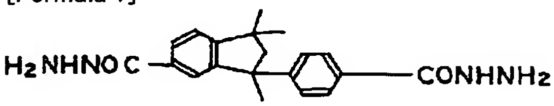
[Formula 6]

$$HO_2C-Ar\left(-Z-Ar\right)_n-CO_2H \quad (6)$$

Ar, Z, and n are the same as that of the contents of said general formula (3) respectively among [general formula (6).]

[Claim 6] 1 expressed with the following type (5), 1, 3-trimethyl-3-phenyl indan - 4', the manufacture approach of the polyoxadiazole derivative characterized by making 5-dicarboxylic acid dihydrazide and the aromatic series dicarboxylic acid expressed with the following general formula (6) react.

[Formula 7]



(5)

[Formula 8]

$$HO_2C-Ar\left(-Z-Ar\right)_n-CO_2H \quad (6)$$

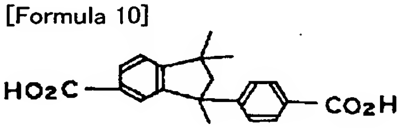
Ar shows a divalent aromatic series radical or a divalent heterocycle type aromatic series radical among [general formula (6), Z is the hydrocarbon group expressed with -CRR- or -CR=CR- (R expresses hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, or the aryl group of carbon numbers 6-30.), and at least one of O, S, and the SO2, and n is the integer of 0, or 1-2.]

[Claim 7] 1 expressed with the aromatic series dicarboxylic acid dihydrazide and the following formula (4) which are expressed with the following general formula (3), 1, 3-trimethyl-3-phenyl indan - 4', the manufacture approach of the polyoxadiazole derivative according to claim 6 characterized by making it react including 5-dicarboxylic acid or either further.

[Formula 9]

$$H_2NHNOC-Ar\left(Z-Ar\right)_n-CONHNH_2 \quad (3)$$

[Formula 10]



(4)

Ar, Z, and n are the same as that of the contents of said general formula (6) respectively among [general formula (3).]

[Claim 8] The manufacture approach of a polyoxadiazole derivative given in any 1 term of claims 4-7 characterized by making it react including further hydrazinium sulfate and hydrochloric-acid hydra JINIUMU, or either.

[Claim 9] The manufacture approach of a polyoxadiazole derivative given in any 1 term of claims 4-8 characterized by making a dihydrazide component and a dicarboxylic acid component react by the mole ratio of 40:60-60:40 (dihydrazide component: dicarboxylic acid component) within the limits.

[Claim 10] the organic electroluminescent element characterized by two or more organic layers containing a luminous layer or the luminous layer concerned concerned being further alike at least in the organic electroluminescent element equipped with two or more organic layers which contain a luminous layer or a luminous layer in inter-electrode [of a pair], and containing the polyoxadiazole derivative of a publication in any 1 term of claims 1-3.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the organic electroluminescent element which used the polyoxadiazole derivative concerned for a polyoxadiazole derivative and its manufacture approach, and a list. It is related with the organic electroluminescent element using the still more nearly meltable polyoxadiazole derivative to the organic solvent concerned about a polyoxadiazole derivative meltable to a more detailed common organic solvent, and its manufacture approach.
[0002]
[Description of the Prior Art] Conventionally, the low-molecular organic compound has been used for the organic electroluminescent element. However, in these components, a low-molecular organic compound may cause degradation to a lifting and a component for crystallization or condensation in connection with the passage of time. If exposed to an elevated temperature by the heat especially generated with a component drive, it will crystallize, therefore component degradation is remarkable. Then, in order to control such component degradation, glass transition temperature is high and using a crystalline low high molecular compound is proposed. Moreover, in order to thin-film-ize a low molecular weight compound, since it is necessary to use means, such as vacuum deposition and the sputtering method, time amount is taken and productivity is bad. On the other hand, a high molecular compound can carry out [thin film]-izing easily by applying a solution. Use of a high molecular compound is called for also from a viewpoint of such a productivity improvement.
[0003] About the electron hole transportation matter, the high molecular compound which was excellent in some is known among the matter which constitutes an organic electroluminescent element. However, about the electronic transportability matter, thing of a certain thing with some sufficient proposals is not yet obtained. the inside of it -- 2-(4-biphenylyl)-5-(4-tert-buthylphenyl)- low-molecular OKISA diazole compounds, such as 1, 3, and 4-OKISA diazole (PBT), are known as an ingredient excellent in the electronic transportability in an organic electroluminescent element -- **** (Jpn.J.Appl.Phys., 27, L269 (1988)) -- some are proposed also about the giant-molecule OKISA diazole compound.
[0004] First, the OKISA diazole compound which has two or more oxadiazole rings in intramolecular is indicated by JP,6-145658,A, JP,6-92947,A, JP,5-152072,A, JP,5-202011,A, and JP,6-136359,A. However, these OKISA diazole compounds of crystallization depressor effect are insufficient, and it gets down also from thin film-ization with vacuum deposition, and the productivity issue is not solved at all.
[0005] Moreover, the OKISA diazole compound which is made to carry out the polymerization of the monomer containing the oxadiazole ring which has the double bond in which a polymerization is possible to an end according to a radical polymerization etc., and is obtained is indicated by JP,8-208745,A and JP,9-255725,A. These OKISA diazole compounds have the oxadiazole ring in the side chain of a giant molecule, and are compounds usable in the electronic transportation layer in an organic electroluminescent element. however, it cannot say that the glass transition temperature of these OKISA diazole compounds is sufficiently high (with a compound given in JP,9-255725,A, it is 179 degrees C), and 10% weight reduction temperature of thermal stability in the inside of nitrogen is inadequate not much highly (**, 394 degrees C) -- etc. -- amelioration of the long term stability of a component is inadequate. Although a high glass transition temperature and thermal stability are expected, since structure becomes upright, generally the polyoxadiazole which repeats and contains an oxadiazole ring in a principal chain cannot melt into an organic solvent easily, and thin-film-izing is difficult for it.
[0006] in order to solve this problem -- "-- Chem.Mater. -- polyoxadiazole is made meltable to an organic solvent by adding a hexafluoro isopropylidene radical to a principal chain, and adding a long-chain alkyl group to a side chain, and closing, if to an organic electroluminescent element is proposed by 1995, 7, and 1568-1575." However, the highest brightness of the organic electroluminescent element using these polyoxadiazole is about 115 cd/m2. It cannot be said with extent that it is not much high. Moreover, although neither glass transition temperature nor weight reduction temperature is indicated, generally, installation of a hexafluoro isopropylidene radical causes the fall of glass transition temperature, and a long-chain alkyl side chain causes not only glass transition temperature but the fall of pyrolysis temperature. Therefore, the viewpoint of the long term stability of a component to these polyoxadiazole is not desirable.
[0007]
[Problem(s) to be Solved] In order to solve the above-mentioned problem, it has the outstanding electronic transport capacity, and it is meltable to an organic solvent, thin-film-izing is easy, and, moreover, development of a

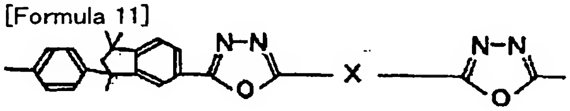
high molecular compound with high thermal stability with high glass transition temperature and pyrolysis temperature has been a technical problem. Then, a header and this invention are completed for having the electronic transport capacity which the artificers of this invention became meltable [polyoxadiazole] to an organic solvent by introducing into intramolecular the OKISA diazole segment which has a phenyl indan radical in a specific joint format as a result of inquiring wholeheartedly, and whose thermal stability was [the polyoxadiazole concerned] high and was moreover excellent.

[0008]

[Means for Solving the Problem] This invention is a polyoxadiazole derivative and is characterized by containing the segment expressed with a general formula (1) to intramolecular.

[0009]

[Formula 11]



(1)

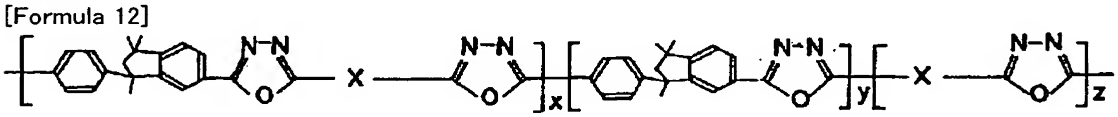
[0010] X is expressed with -Ar-(Z-Ar) n- among [type (1), and Ar shows a divalent aromatic series radical or a divalent heterocycle type aromatic series radical among the X concerned. Z - CRR- or -CR=CR - (R expresses hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, and the aryl group of carbon numbers 6-30.) it is the hydrocarbon group expressed and at least one of O (oxygen atom), S (sulfur atom), and the SO2 (sulfur dioxide), and n is the integer of 0, or 1-2.]

[0011] Thus, by containing in intramolecular the OKISA diazole segment which has a phenyl indan radical in a specific joint format, a meltable polyoxadiazole derivative can be offered to common organic solvents, such as dichloromethane, chloroform, 1,1,2,2-tetrachloroethane, a dichloroethane, or N-methyl pyrrolidone (NMP may be called hereafter).

[0012] Moreover, in constituting a polyoxadiazole derivative, it is desirable that the polyoxadiazole derivative containing the segment expressed with a general formula (1) is the compound (structure) expressed with the following general formula (2).

[0013]

[Formula 12]



(2)

[0014] Among [general formula (2), Ar, Z, and n are the respectively same contents as a general formula (1), the mole ratio of x:y is the value of 100:0-100:1000 within the limits, and the mole ratio of x:z is the value of 100:0-100:500 within the limits.]

[0015] Thus, by constituting a polyoxadiazole derivative, a polyoxadiazole derivative can be more easily dissolved to common organic solvents, such as dichloromethane, 1,1,2,2-tetrachloroethane, etc. which were mentioned above. Therefore, it is at least 1% of the weight or more of concentration, with a polyoxadiazole derivative can be dissolved.

[0016] moreover, a polyoxadiazole derivative -- constituting -- hitting -- the logarithm of the polyoxadiazole derivative concerned -- it is desirable to make viscosity etainh (Measuring condition: the temperature of 30 degrees C, a solvent sulfuric acid, concentration 0.5 g/dl) into the value of 0.1 - 2 dl/g within the limits. such range -- the logarithm of a polyoxadiazole derivative -- viscosity etainh While being able to dissolve the polyoxadiazole derivative concerned in a common organic solvent easily by restricting a value, the uniform thin film excellent in thermal resistance can be formed. Therefore, when the polyoxadiazole derivative concerned is used for the luminous layer in an organic electroluminescent element etc., it excels in endurance, and charge transportability is high and can obtain the organic electroluminescent element of high luminous efficiency.

[0017] Moreover, another mode of this invention is a 1 expressed in following formula (4) as aromatic series dicarboxylic acid dihydrazide which is manufacture approach of polyoxadiazole derivative and is expressed with following general formula (3), 1, and 3-trimethyl-3-phenyl indan. - It is characterized by 4' and making 5-dicarboxylic acid react (the 1st approach).

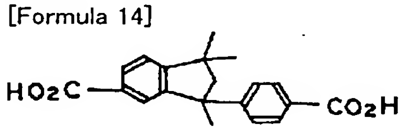
[0018]

[Formula 13]

$$H_2NHNOC-Ar-\left(Z-Ar\right)_n-CONHNH_2 \qquad (3)$$

[0019]

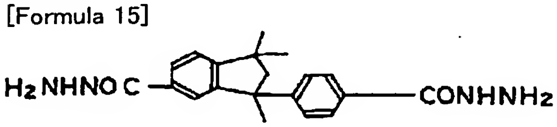
[Formula 14]



(4)

[0020] Ar shows a divalent aromatic series radical or a divalent heterocycle type aromatic series radical among

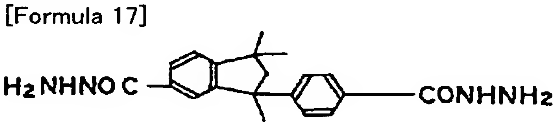
[general formula (3), Z is the hydrocarbon group expressed with -CRR- or -CR=CR- (R expresses hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, or the aryl group of carbon numbers 6-30.), and at least one of O, S, and the SO2, and n is the integer of 0, or 1-2.]
[0021] thus, the thing for which the polyoxadiazole derivative of this invention is manufactured -- a polyoxadiazole derivative meltable to common organic solvents, such as 1,1,2,2-tetrachloroethane, -- being efficient (high recovery) -- it can manufacture.
[0022] Moreover, 1 which is expressed with the following formula (5) in enforcing the manufacture approach (the 1st approach) of the polyoxadiazole derivative in this invention, 1, a 3-trimethyl-3-phenyl indan - It is desirable to make it react including further 4', the aromatic series dicarboxylic acid expressed with 5-dicarboxylic acid dihydrazide and the following general formula (6), or either.
[0023]
[Formula 15]


(5)

[0024]
[Formula 16]

$$HO_2C-Ar\left(-Z-Ar\right)_n CO_2H \quad (6)$$

[0025] Ar, Z, and n are the same as that of the contents of said general formula (3) respectively among [general formula (6).]
[0026] thus, the thing for which the polyoxadiazole derivative of this invention is manufactured -- a polyoxadiazole derivative meltable to common organic solvents, such as 1,1,2,2-tetrachloroethane, -- being efficient (high recovery) -- it can manufacture.
[0027] Moreover, another mode of this invention is a 1 which is manufacture approach of polyoxadiazole derivative and is expressed with following formula (5), 1, and 3-trimethyl-3-phenyl indan. - It is characterized by making 4', and 5-dicarboxylic acid dihydrazide and the aromatic series dicarboxylic acid expressed with the following general formula (6) react (the 2nd approach).
[0028]
[Formula 17]


(5)

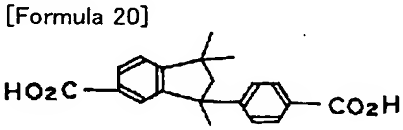
[0029]
[Formula 18]

$$HO_2C-Ar\left(-Z-Ar\right)_n CO_2H \quad (6)$$

[0030] Ar, Z, and n are the same as that of the contents of said general formula (3) respectively among [general formula (6).]
[0031] thus, the thing for which the polyoxadiazole derivative of this invention is manufactured -- a polyoxadiazole derivative meltable to common organic solvents, such as 1,1,2,2-tetrachloroethane, -- being efficient (high recovery) -- it can manufacture.
[0032] Moreover, 1 which is expressed with the aromatic series dicarboxylic acid dihydrazide and the following formula (4) which are expressed with the following general formula (3) in enforcing the manufacture approach (the 2nd approach) of the polyoxadiazole derivative in this invention, 1, a 3-trimethyl-3-phenyl indan - It is desirable 4' and to make it react including 5-dicarboxylic acid or either further.
[0033]
[Formula 19]

$$H_2NHNOC-Ar\left(-Z-Ar-\right)_n CONHNH_2 \quad (3)$$

[0034] Ar, Z, and n are the same as that of the contents mentioned above, respectively among [general formula (3).]
[0035]
[Formula 20]


(4)

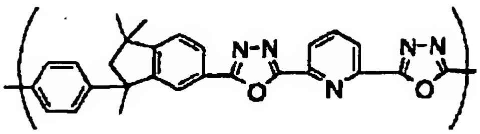
[0036] thus, the thing for which the polyoxadiazole derivative of this invention is manufactured — a polyoxadiazole derivative meltable to common organic solvents, such as 1,1,2,2-tetrachloroethane, — being efficient (high recovery) — it can manufacture.
[0037] Moreover, in enforcing the manufacture approach (the 1st and 2nd approaches) of the polyoxadiazole derivative in this invention, it is desirable to make it react including further hydrazinium sulfate and hydrochloric-acid hydra JINIUMU, or either. Thus, by manufacturing a polyoxadiazole derivative including hydrazinium sulfate or hydrochloric-acid hydra JINIUMU, the content of an OKISA diazole radical can be prepared easily. Therefore, a meltable polyoxadiazole derivative can be manufactured more efficiently (high recovery) quantitatively to common organic solvents, such as 1,1,2,2-tetrachloroethane.
[0038] Moreover, in enforcing the manufacture approach (the 1st and 2nd approaches) of the polyoxadiazole derivative in this invention, it is desirable to be each total amount, with to be the mole ratio of 40:60-60:40 (dihydrazide component: dicarboxylic acid component) within the limits, and to make a dihydrazide component and a dicarboxylic acid component react especially by the mole ratio of 45:55-55:45 (dihydrazide component: dicarboxylic acid component) within the limits. In addition, a dihydrazide component shows the compound expressed with a general formula (3), the compound expressed with a general formula (5), hydrochloric-acid hydra JINIUMU, and hydrazinium sulfate. Moreover, a dicarboxylic acid component shows the compound, hydrochloric-acid hydra JINIUMU, and hydrazinium sulfate which are expressed with a general formula (4) and a general formula (5).
[0039] moreover, another mode of this invention is characterized by two or more organic layers containing a luminous layer or a luminous layer concerned being further alike at least, and containing the polyoxadiazole derivative mentioned above in the organic electroluminescent element equipped with two or more organic layers which contain a luminous layer or a luminous layer in inter-electrode [of a pair].
[0040] By having the outstanding charge transportability, therefore constituting an organic electroluminescent element in this way, the polyoxadiazole derivative mentioned above can demonstrate the outstanding charge transportability, and can offer an organic electroluminescent element with a quick speed of response.
[0041] Moreover, since it can be made to dissolve in common organic solvents, such as 1,1,2,2-tetrachloroethane, easily, when producing an organic electroluminescent element, the polyoxadiazole derivative of this invention is easy handling, and it can use it as a uniform thin film.
[0042] Furthermore, in constituting the organic electroluminescent element of this invention, it is desirable to contain the polyoxadiazole derivative of this invention which used one of the organic layers as the charge transportation layer (electronic transportation layer), and was mentioned above in the charge transportation layer (electronic transportation layer) concerned. Thus, by constituting an organic electroluminescent element, the outstanding charge transportability (electronic transportability) which the polyoxadiazole derivative of this invention has can be demonstrated more efficiently, and the organic electroluminescent element of high luminous efficiency can be offered.
[0043]
[Embodiment of the Invention] Hereafter, the operation gestalten 1-3 of this invention are explained more concretely. First, the 1st operation gestalt of this invention is a polyoxadiazole derivative, and is characterized by including the OKISA diazole segment which is expressed with said general formula (1) and which has a phenyl indan radical.
[0044] Moreover, in order to acquire the fusibility over a higher organic solvent, it is desirable that the OKISA diazole segment which does not have the segment and phenyl indan radical which the phenyl indan radical and the oxadiazole ring coupled directly is included in intramolecular random or in the shape of a block with the OKISA diazole segment which has a phenyl indan radical so that it may be expressed with said general formula (2).
[0045] However, the OKISA diazole segment which does not have the segment and phenyl indan radical which the phenyl indan radical and the oxadiazole ring coupled directly is easy to contain either, respectively. In that case, when [of the OKISA diazole segment which has a phenyl indan radical] (x) is comparatively made into 100 mols, it is desirable to make [of the OKISA diazole segment in which making / of the segment which the phenyl indan radical and the oxadiazole ring coupled directly / (y) into the value within the limits of 0-1000 mols comparatively does not have a phenyl indan radical similarly preferably] (z) into the value within the limits of 0-500 mols comparatively.
[0046] Making Ar into the aromatic series radical of bivalence or the heterocycle type aromatic series radical of bivalence among a general formula (1) and a general formula (2) here has good reactivity if it is these radicals, when manufacturing a polyoxadiazole derivative, and it is because it can consider as the thin film of the polyoxadiazole derivative which raised the glass transition temperature of the polyoxadiazole derivative obtained, and was excellent in endurance or thermal resistance.
[0047] Moreover, they are the inside of a general formula (1) and a general formula (2), and Z -CRR- or -CR=CR - (R) hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, or the aryl group of carbon numbers 6-30 is expressed. A hydrocarbon group, and O, S and SO2 which are expressed If it is these radicals, it will be referred to as at least one because reactivity when manufacturing a polyoxadiazole derivative is good.
[0048] Furthermore, with [reactivity / reactivity if it is this integer, when manufacturing a polyoxadiazole derivative is good, and] such a raw material, the several n repeat in a general formula (1) and a general formula (2) is made into the integer of 0, or 1-2 because it is easily available.

[0049] Furthermore, if it is the value of this within the limits, make the mole ratio of x:y into the value of 100:0-100:1000 within the limits among a general formula (2), and because the obtained OKISA diazole derivative becomes meltable to an organic solvent, let the mole ratio of x:z be the value of 100:0-100:500 within the limits.
[0050] Moreover, in the polyoxadiazole derivative of this invention, it is desirable to make glass transition temperature (Tg) of the polyoxadiazole derivative concerned into the value of 200 degrees C or more. Thus, by controlling the value of glass transition temperature (Tg) and constituting a polyoxadiazole derivative, it is because it excels in thermal resistance etc. and a possibility of crystalizing can obtain the polyoxadiazole derivative of few thin films. And the glass transition temperature (Tg) of a more desirable polyoxadiazole derivative is 250 degrees C or more in value, and is 300 degrees C or more in value the optimal. In addition, the glass transition temperature (Tg) of the polyoxadiazole derivative concerned can be measured in a nitrogen air current using DSC (Differential Scanning Calorimeter).
[0051] Moreover, in the polyoxadiazole derivative of this invention, it is desirable to make decrease pyrolysis temperature of 5% weight of the polyoxadiazole derivative concerned (Td5) into the value of 200 degrees C or more from a viewpoint which can obtain the polyoxadiazole derivative excellent in thermal resistance, endurance, etc. And the more desirable decrease pyrolysis temperature of 5% weight of a polyoxadiazole derivative (Td5) is 250 degrees C or more in value, and is 300 degrees C or more in value the optimal. In addition, the decrease pyrolysis temperature of 5% weight of the polyoxadiazole derivative concerned (Td5) can be measured, using TGA (Thermal GravityAnalyzer) as temperature at the time of weight decreasing 5% from an initial mass.
[0052] moreover, molecular weight although it has sufficient thermal resistance and endurance even if the end closure of the polyoxadiazole derivative of this invention is not carried out, in order that it may raise thermal resistance and endurance further -- adjusting -- a suitable logarithm -- in order to consider as viscosity, end encapsulant may be used and end closure of the end of a polyoxadiazole derivative derivative may be carried out.
[0053] Here, as usable end encapsulant, kinds, such as hydrazides of aromatic series monocarboxylic acid, such as a benzoic acid, 1-naphthoic acid, 2-naphthoic acid, 4-biphenyl carboxylic acid, and 2-pyridinecarboxylic acid, or these aromatic series monocarboxylic acid, or two sorts or more are mentioned. And it is desirable to make the amount of this end encapsulant used into the value within the limits of 0.001-0.25 mols per one mol of polyoxadiazole derivatives.
[0054] moreover, the logarithm of the viewpoint which is excellent in thermal resistance and can be used as a uniform thin film in the polyoxadiazole derivative of this invention while being able to make it dissolve in a common organic solvent easily to a polyoxadiazole derivative -- it is desirable to make viscosity etainh (Measuring condition: the temperature of 30 degrees C, a solvent sulfuric acid, concentration 0.5 g/dl) into the value of 0.1 - 2.0 dl/g within the limits.
[0055] and the logarithm of a viewpoint with the better balance of the solubility over an organic solvent, and thermal resistance and uniform film production nature to a polyoxadiazole derivative -- viscosity etainh It is considering as the value of 0.6 - 1.2 dl/g within the limits more preferably [considering as the value of 0.5 - 1.5 dl/g within the limits], and the optimal.
[0056] Next, the 2nd operation gestalt of this invention is explained. The aromatic series dicarboxylic acid dihydrazide which this 2nd operation gestalt is the efficient manufacture approach of a polyoxadiazole derivative, and is expressed with said general formula (3), 1 expressed with said general formula (4), 1, 3-trimethyl-3-phenyl indan - (the 1st approach) [4' and] [whether 5-dicarboxylic acid is made to react and] Or 1 expressed in said formula (6) as the aromatic series dicarboxylic acid expressed with said general formula (5), 1, a 3-trimethyl-3-phenyl indan - It is characterized by 4' and the thing which you make 5-dicarboxylic acid dihydrazide react (the 2nd approach).
[0057] Here, it is -CRR about the reason and Z which make Ar the aromatic hydrocarbon radical of bivalence, or the heterocycle type aromatic series radical of bivalence among a general formula (3) and a general formula (5). - (R) hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, and the aryl group of carbon numbers 6-30 are expressed. A hydrocarbon group, and O, S and SO2 which are expressed The reason for making into the integer of 0, or 1-2 the reason set to at least one and a several n repeat is the same as the reason explained by the general formula (1) and the general formula (2), respectively.
[0058] moreover, in enforcing the manufacture approach (the 1st approach) of the polyoxadiazole derivative in this invention, as aromatic series dicarboxylic acid dihydrazide expressed with a general formula (3) Phthalic-acid dihydrazide, terephthalic-acid dihydrazide, isophthalic acid dihydrazide, 1, 4-naphthalene dicarboxylic acid dihydrazide, 2, 3-naphthalene dicarboxylic acid dihydrazide, 2, 6-naphthalene dicarboxylic acid dihydrazide, 2, 3-pyridine dicarboxylic acid dihydrazide, 2, 4-pyridine dicarboxylic acid dihydrazide, 2, 5-pyridine dicarboxylic acid dihydrazide, 2,6-pyridine-dicarboxylic-acid dihydrazide, 3, 5-pyridine dicarboxylic acid dihydrazide, - biphenyl dicarboxylic acid dihydrazide, and 2 and 2 '4, 4'-biphenyl dicarboxylic acid dihydrazide, 9-full -- me -- non -2, 7-dicarboxylic acid dihydrazide, a stilbene -4, and 4'-dicarboxylic acid dihydrazide -- - JIHIDORAJINO carbonyl diphenyl ether, and 4 and 4 '4, 4'-JIHIDORAJINO carbonyl diphenylsulfone, A 4 and 4'-JIHIDORAJINO carbonyl diphenyl sulfide, It is desirable to use at least one aromatic series dicarboxylic acid dihydrazide chosen from the group which consists of a 2 and 2-screw (4-hydrazino carbonyl phenyl) hexafluoropropane and 2, and 2-screw (4-hydrazino carbonyl phenyl) propane. These aromatic series dicarboxylic acid dihydrazide is a 1, 1, and 3-trimethyl-3-phenyl indan. - Reactivity with 4' and 5-dicarboxylic acid is good, and recovery high about a polyoxadiazole derivative is acquired, and acquisition is also because it is easy.
[0059] Moreover, 1 which is expressed in a formula (4) as the aromatic series dicarboxylic acid dihydrazide

expressed with a general formula (3) in enforcing the manufacture approach (the 1st approach) of the polyoxadiazole derivative in this invention, 1, a 3-trimethyl-3-phenyl indan - In making 5-dicarboxylic acid react, it is desirable 4' and to make the reaction mole ratio concerned into the value of 40:60-60:40 within the limits. By making a reaction mole ratio into the value of this within the limits, it is for the reaction at the time of manufacturing about [that the obtained OKISA diazole derivative becomes meltable to an organic solvent certainly] and an OKISA diazole derivative to arise certainly, and for the amount of unreacted components to decrease.
[0060] Therefore, 1 expressed in a formula (4) as the aromatic series dicarboxylic acid dihydrazide expressed with the general formula (3) which hits enforcing the 1st approach, 1, a 3-trimethyl-3-phenyl indan - More preferably, the reaction mole ratio with 5-dicarboxylic acid is the value of 45:55-55:45 within the limits, and are 4' and considering as the value of 48:52-52:48 within the limits the optimal.
[0061] moreover, in enforcing the manufacture approach (the 2nd approach) of the polyoxadiazole derivative in this invention, as aromatic series dicarboxylic acid expressed with a general formula (5) A phthalic acid, a terephthalic acid, isophthalic acid, 1, 4-naphthalene dicarboxylic acid, 2, 3-naphthalene dicarboxylic acid, 2, 6-naphthalene dicarboxylic acid, 2, 3-pyridine dicarboxylic acid, 2, 4-pyridine dicarboxylic acid, 2, 5-pyridine dicarboxylic acid, 2,6-pyridine-dicarboxylic-acid, 3, 5-pyridine dicarboxylic acid, 4, and 4'-biphenyl dicarboxylic acid, 2 and 2'-biphenyl dicarboxylic acid and 9-full -- me -- non -2 and 7-dicarboxylic acid -- A stilbene -4, - dicarboxylic acid, and 4 '4, 4'-dicarboxy diphenyl ether, A - dicarboxy diphenylsulfone, and 4 and 4 '4, 4'-dicarboxy diphenyl sulfide, It is desirable to use at least one aromatic series dicarboxylic acid chosen from the group which consists of a 2 and 2-screw (4-carboxyphenyl) hexafluoropropane and 2, and 2-screw (4-carboxyphenyl) propane. These aromatic series dicarboxylic acid is a 1, 1, and 3-trimethyl-3-phenyl indan. - Reactivity with 4', 5-dicarboxylic acid dihydrazide, etc. is good, and recovery high about a polyoxadiazole derivative is acquired, and the acquisition itself is because it is easy.
[0062] Moreover, 1 which is expressed in a formula (6) as the aromatic series dicarboxylic acid expressed with a general formula (5) in enforcing the manufacture approach (the 2nd approach) of the polyoxadiazole derivative in this invention, 1, a 3-trimethyl-3-phenyl indan - It is desirable 4' and to make a reaction mole ratio with 5-dicarboxylic acid dihydrazide into the value of 40:60-60:40 within the limits. By making a reaction mole ratio into the value of this within the limits, it is for the reaction at the time of manufacturing about [that the obtained OKISA diazole derivative becomes meltable to an organic solvent certainly] and an OKISA diazole derivative to arise certainly, and for the amount of unreacted components to decrease.
[0063] Therefore, 1 which is expressed in a formula (6) as the aromatic series dicarboxylic acid expressed with a general formula (5) in enforcing the 2nd approach, 1, a 3-trimethyl-3-phenyl indan - It is 4' and being the value of 45:55-55:45 within the limits, and making more preferably, a reaction mole ratio with 5-dicarboxylic acid dihydrazide into the value of 48:52-52:48 within the limits the optimal. In addition, in the manufacture approach of this invention, when calling it the amount of a dicarboxylic acid component and the dihydrazide component used, the total amount of a dicarboxylic acid component and the total amount of a dihydrazide component are said, respectively. Moreover, when hydrazinium sulfate and hydrochloric-acid hydra JINIUMU are used, these hydra JINIUMU is converted as a dihydrazide component.
[0064] Moreover, in enforcing the manufacture approach (the 1st and 2nd approaches) which is the 2nd operation gestalt of this invention, it is desirable to use a condensing agent. Namely, the aromatic series dicarboxylic acid dihydrazide expressed with said general formula (3), 1 expressed with said formula (4), 1, 3-trimethyl-3-phenyl indan - (the 1st approach) [4' and] [whether 5-dicarboxylic acid is made to react under existence of a condensing agent, and] Or 1 expressed in said formula (6) as the aromatic series dicarboxylic acid expressed with said general formula (5), 1, a 3-trimethyl-3-phenyl indan - 4' and the thing which you make 5-dicarboxylic acid dihydrazide react under existence of a condensing agent (the 2nd approach) are desirable. Thus, by using a condensing agent, a polyoxadiazole derivative can be manufactured more efficiently (high recovery) quantitatively.
[0065] Here, the class of condensing agent to be used cannot be asked, for example, can use Pori phosphoric acid etc. Moreover, it is more desirable to use the mixture of 5 oxidation **** and methansulfonic acid as a condensing agent from a viewpoint which can produce the reaction of hydrazide and a carboxylic acid alternative moreover very efficiently.
[0066] and the case where the mixture of 5 oxidation **** and methansulfonic acid is used -- the mixing ratio of the 5 oxidation **** concerned and methansulfonic acid -- although especially a rate is not asked, either, it is desirable to make methansulfonic acid into the value of the 300 - 3000 weight section within the limits to the 5 oxidation **** 100 weight section from a viewpoint in which the more excellent condensation effectiveness can be demonstrated and an excessive condensing agent does not remain. And it is desirable to heat the mixture of 5 oxidation **** and methansulfonic acid beforehand in a 50-150-degree C temperature requirement, and to dissolve 5 oxidation **** into methansulfonic acid from a viewpoint which can demonstrate the further excellent condensation effectiveness.
[0067] Moreover, in enforcing the manufacture approach (the 1st and 2nd approaches) of this invention, reaction temperature is made into the value within the limits of 50-150 degrees C from a viewpoint which can manufacture the polyoxadiazole derivative of this invention more efficiently and certainly, and it is desirable to carry out a condensation reaction for 2 to 72 hours. And more preferably, reaction temperature is made into the value within the limits of 80-120 degrees C, and it is the thing for 5 to 72 hours to do for a condensation reaction.
[0068] Finally, the 3rd operation gestalt of this invention is explained. this 3rd operation gestalt is the organic electroluminescent element which used the polyoxadiazole derivative, and is characterized by having two or more

organic layers which contain a luminous layer or a luminous layer in inter-electrode [of a pair], and for two or more organic layers containing a luminous layer or a luminous layer concerned being further alike at least, and containing the polyoxadiazole derivative mentioned above.
[0069] Here, various kinds of modes can be taken as a configuration of an organic electroluminescent element. For example, the configuration which formed the luminous layer in inter-electrode [of a pair] (an anode plate and cathode), the configuration which formed the luminous layer and the electron hole (hole) transportation layer in inter-electrode [of a pair] (an anode plate and cathode), The configuration which formed the luminous layer and the electronic (electron) transportation layer in inter-electrode [of a pair] (an anode plate and cathode), It can consider as the configuration which formed the electron hole transportation layer, the luminous layer, and the electronic transportation layer in inter-electrode [of a pair] (an anode plate and cathode), or the configuration which formed the electron injection layer and the hole-injection layer in contact with the electrode further. Namely, what is necessary is just the configuration of the organic electroluminescent element equipped with two or more organic layers which contain a luminous layer or a luminous layer in inter-electrode [of a pair].
[0070] In addition, it is also possible to form a glass substrate and a plastics base material in a lower part (inferior surface of tongue) side as a supporting material of the component in these organic electroluminescent elements if needed.
[0071] And the case where a luminous layer is formed in inter-electrode [of a pair] (an anode plate and cathode) among the configurations in these organic electroluminescent elements is concretely explained using drawing 1 .
[0072] The laminating of the organic electroluminescent element 10 in drawing 1 is carried out, and the order of a glass substrate 1, the ITO film (anode plate) 2, the luminous layer 3 containing a polyoxadiazole derivative, and the aluminum layer (cathode) 4 constitutes it from the lower part. This organic electroluminescent element 10 is electrically connected to external DC power supply 5 through the ITO film (anode plate) 2 vapor-deposited and formed on the glass substrate 1, and the aluminum layer (cathode) 4 which similarly vapor-deposited and was formed.
[0073] Therefore, if an electrical potential difference is impressed from external DC power supply 5, an electron will be poured in from the aluminum layer (cathode) 4, and this electron will be sent to a luminous layer 3. On the other hand, if an electrical potential difference is impressed from DC power supply 5, an electron hole (hole) will be poured in from the ITO film (anode plate) 2, and this electron hole will be sent to a luminous layer 3. That is, in a luminous layer 3, an electron and an electron hole recombine and recombination energy is emitted. Therefore, this recombination energy will be emitted as an electroluminescence light.
[0074] In addition, in order to use the recombination energy of this electron and electron hole more efficiently, it is also possible to include photogene in a luminous layer 3, to excite photogene with the recombination energy concerned, and to emit light as electroluminescence.
[0075] Moreover, although especially the thickness of two or more organic layers (for example, electron hole transportation layer) containing a luminous layer 3 or a luminous layer is not restricted, it is considering as the value within the limits of 10nm - 200nm preferably [usually making thickness per layer into the value within the limits of 1nm - 1000nm], and more preferably.
[0076] In addition, since it is possible to apply the polyoxadiazole derivative of the amount of giant molecules concerned using the organic solvent of a low-boiling point when forming the polyoxadiazole derivative of this invention as one of two or more of the organic layers containing a luminous layer or a luminous layer, a uniform thin film can be formed rather than there are few defects of a pinhole etc.
[0077] Moreover, as an ingredient of the anode plate 2 in the organic electroluminescent element 10 with which it was expressed to drawing 1 , although the indium-tin-oxide compound (ITO) is used, if it is a large (4eV or more as an example) metal, an alloy or an oxide conductor of a work function, etc., it is usable. And as a concrete ingredient, the use of transparence oxide conductors, such as alloys, such as metals, such as Au, and Au/nickel, or a diacid-ized tin compound (SnO_2), and a zinc oxide (ZnO), other than the indium-tin-oxide compound (ITO) mentioned above is desirable.
[0078] Moreover, since taking out luminescence from the anode plate side of an organic electroluminescent element generally is performed, as an ingredient of the anode plate concerned, a transparent electrode ingredient is desirable, therefore it is optimal to use the transparence oxide conductor mentioned above as an anode material.
[0079] In addition, it will go caudad, electroluminescence light will be emitted and it enables it to have taken out electroluminescence light outside through the ITO film 2 and a glass substrate 1 in the organic electroluminescent element 10 of a configuration of being shown in drawing 1 .
[0080] moreover -- although especially the thickness of an anode plate is not what is limited -- from a viewpoint with the good balance of transparency and membranous homogeneity -- usually -- the range of 10-1000nm -- it is more preferably chosen within the limits of 10-200nm. Furthermore, although especially the process of an anode plate is not limited, either, it can form by the general technique, such as vacuum evaporationo and sputtering.
[0081] As an ingredient of the cathode 4 in the organic electroluminescent element 10 with which it was expressed to drawing 1 on the other hand, a small (less than 4eV as an example) metal, an alloy or a conductive compound of a work function, etc. is desirable. Although aluminum is used in this example, it is also desirable to use alloys, such as metals, such as calcium, magnesium, a lithium, and an indium, an aluminium alloy, a calcium alloy, a Magnesium alloy, and a lithium alloy.
[0082] in addition -- although it is not what is especially limited also about the thickness of cathode -- from a viewpoint with the good balance of internal resistance and membranous homogeneity -- usually -- the range of 10-

1000nm — it is more preferably chosen within the limits of 50-200nm. Moreover, although especially the process of cathode is not limited, either, it can form by the general technique, such as vacuum evaporationo and sputtering, like an anode plate.
[0083] Moreover, in constituting the organic electroluminescent element 10 mentioned above, as mentioned above, it is desirable to contain the polyoxadiazole derivative of this invention in a luminous layer 3 (for it to be an electronic transportation layer separately, when the electronic transportation layer is prepared) from a viewpoint which can be made to be able to demonstrate more efficiently the outstanding electronic transportability which a polyoxadiazole derivative has, and can offer an organic electroluminescent element with a speed of response quick further more.
[0084] And preferably [considering as at least 10 % of the weight or more] as a content of a polyoxadiazole derivative, and more preferably, it is 50 % of the weight or more, and is 90% of the weight or more of a value the optimal. When the content of a polyoxadiazole derivative becomes less than 10 % of the weight, it is because there is a possibility that electronic transportability may fall remarkably.
[0085] In addition, the polymeric materials for raising film production nature besides the luminescent material mentioned later as ingredients other than the polyoxadiazole derivative in a luminous layer 3, the compound which has one or more oxadiazole rings in which structure differs from the polyoxadiazole derivative of this invention for raising electronic transportability more, a diphenyl quinone derivative and a thiophene derivative, a triazole derivative, a thiadiazole derivative, a quinoxaline derivative, a phenanthroline derivative, etc. are mentioned.
[0086] In constituting the organic electroluminescent element 10 mentioned above moreover, in the electron hole transportation layer 2 A polyvinyl carbazole (PVCZ), N-phenyl carbazole, Pori (p-phenylenevinylene), N, N'-diphenyl-N, N'-JI (3-methylphenyl) -4, a 4'-diamino biphenyl (TPD), One, such as 1 and 1-screw (4-G p-tolylamino phenyl) cyclohexane, N, N'-diphenyl-N, N'-dinaphthyl -4, a 4'-diamino biphenyl, a phthalocyanine derivative, and polysilane, or two or more are usable.
[0087] Moreover, in constituting the organic electroluminescent element 10 mentioned above, as a luminescent material in a luminous layer 3, can use well-known ingredients, such as a daylight fluorescence ingredient, a fluorescent brightener, laser coloring matter, and an organic scintillator, but More specifically An anthracene, a phenanthrene, a pyrene, a chrysene, Perylene, coronene, rubrene, Quinacridone, quarter phenyl, 1, 4-screw (2-methyl styryl) benzene, 1, 4-screw (4-methyl styryl) benzene, One or two compounds or more, such as 1, 4-screw (4-methyl-5-phenyl-2-oxazolyl) benzene, 2, 5-screw (5-tertiary butyl-2-benzoxazolyl) thiophene, 1, 4-diphenyl-1,3-butadiene, and a metal complex, are mentioned.
[0088] Although the configuration (organic electroluminescent element) of the 3rd operation gestalt [in / the above passage / this invention] was explained about the case where a luminous layer is formed in inter-electrode [of a pair] (an anode plate and cathode), using drawing 1 as an example The configuration which formed the luminous layer and the electron hole (hole) transportation layer in inter-electrode [of a pair] (an anode plate and cathode), The same ingredient and the thickness range are employable with having already explained to inter-electrode [of the configuration which formed the luminous layer and the electronic (electron) transportation layer in inter-electrode / of a pair / (an anode plate and cathode), and a pair] (an anode plate and cathode) also in the configuration in which the electron hole transportation layer, the luminous layer, and the electronic transportation layer were formed etc.
[0089]
[Example] Hereafter, this invention is more concretely explained based on an example. However, although it is needless to say, the following publications do not explain this invention generally and this invention is not limited by this publication without a special reason.
[0090] (Example 1)
(Manufacture of a polyoxadiazole derivative) It heated at 100 degrees C, having held 22ml methansulfonic acid and 3.6g 5 oxidation **** in 100ml flask, and agitating the inside of a flask in it using a stirrer. And 5 oxidation **** was dissolved to methansulfonic acid, and it considered as the condensing agent solution. Next, to this condensing agent solution, a mole ratio 1:1 comes out comparatively, with it is a 1.117g (3.44mmol) 1, 1, and 3-trimethyl-3-phenyl indan. - 4', 5-dicarboxylic acid, and 0.6714g (3.44mmol) 2,6-pyridine-dicarboxylic-acid dihydrazide were added.
[0091] And agitating the inside of a flask using a stirrer, at the temperature of 120 degrees C, the condensation reaction was performed about these reaction raw materials, and reaction mixture was obtained for 11 hours. Next, after cooling the temperature in a flask to a room temperature, underwater [in a beaker / about 300ml] was filled with the obtained reaction mixture, and the powdery solid-state product was deposited. And the obtained solid-state product was carried out the ** exception using the filter paper, it is water, a sodium-hydrogencarbonate water solution, water, and a methanol, with sequential washing was carried out. Then, the vacuum drying of the obtained solid-state product was carried out.
[0092] Consequently, the weight of the obtained solid-state product (P1 may be called hereafter) was 1.52g, and recovery was very as high as 99%. Moreover, when infrared spectroscopy measurement was performed to the obtained solid-state product, the wave numbers 2956, 1612, and 1577 and a peak characteristic of 1544cm-1 were acquired, and it was checked that the polyoxadiazole derivative shown in a bottom type (7) is manufactured. In addition, the IR spectrum measured to drawing 1 is shown. This IR spectrum takes the wave number (cm-1) on an axis of abscissa, is shown on it, takes permeability (%) on an axis of ordinate, and is shown on it.
[0093]
[Formula 21]



(7)

[0094] moreover, the logarithm of the obtained polyoxadiazole derivative — when viscosity etainh (Measuring condition: the temperature of 30 degrees C, a solvent sulfuric acid, concentration of 0.5g / dl) was measured, the value of 0.39 dl/g was acquired. Moreover, when the glass transition temperature (Measuring condition: programming-rate 10degree C/min., nitrogen air current) of the obtained polyoxadiazole derivative was measured using DSC, the high value of 332 degrees C was acquired. Furthermore, when the decrease pyrolysis temperature of 5% weight of the obtained polyoxadiazole derivative (Measuring condition: programming-rate 10degree C/min.) was measured using TGA, the high value of 442 degrees C was acquired.
[0095] (Preparation of a polyoxadiazole derivative solution) About the obtained solid-state product, the dissolution sex test to various solvents was performed, preparing a polyoxadiazole derivative solution. That is, to 1,1,2,2-tetrachloroethane, chloroform, dichloromethane, and NMP, when [of a room temperature (25 degrees C) and 1 - 5 % of the weight of concentration] it came out comparatively, with was made to dissolve, the transparent polyoxadiazole derivative solution was able to be altogether prepared for the polyoxadiazole derivative. A result is shown in Table 3.
[0096] In addition, O mark in Table 3 shows the case of 5 % of the weight of concentration where it was able to come out comparatively, with a transparent polyoxadiazole derivative solution is able to be prepared, it comes out comparatively, with ** mark shows the case of 5 % of the weight of concentration where a polyoxadiazole derivative solution is able to be prepared, although it is opaque a part, and even if x mark is the rate of 1 % of the weight of concentration, it shows the case where a polyoxadiazole derivative solution is not able to be dissolved. Hereafter, the same decision criterion estimated solubility.
[0097] Therefore, the obtained polyoxadiazole derivatives are 1,1,2,2-tetrachloroethane, chloroform, dichloromethane, and the common organic solvent of NMP, and it was checked that the solubility (fusibility may be called) which was excellent to the organic solvent of a low-boiling point is shown so that I might be easily understood from the result of Table 3.
[0098] (Measurement of a fluorescence spectrum) Using the 1,1,2,2-tetrachloroethane solution (10 % of the weight of concentration) of a polyoxadiazole derivative, it is the cast method, with the thin film with a thickness of 20 micrometers was formed on the glass plate. And blue fluorescence was emitted when ultraviolet rays were irradiated to the thin film of the polyoxadiazole derivative which carried out in this way and was formed. And when the fluorescence spectrum was measured, it is peak wavelength lambdamax. It carried out and the value of 383nm was acquired. Therefore, when the thin film of the polyoxadiazole derivative concerned is used for the luminous layer of an organic electroluminescent element, emitting light near 383nm is presumed.
[0099]
[Table 1]

ポリオキサジアゾール誘導体の製造

	ジカルボン酸(使用量)	ジヒドラジド化合物(使用量)
実施例1	1, 1, 3-トリメチル-3-フェニルインダン-4', 5-ジカルボン酸(1. 117g、3. 44 mmol)	2, 6-ピリジンジカルボン酸ジヒドラジド (0. 6714g、3. 44mmol)
実施例2	〃	テレフタル酸ジヒドラジド (0. 6679g、3. 44 mmol)
実施例3	〃	イソフタル酸ジヒドラジド (0. 6679g、3. 44 mmol)
実施例4	〃	2, 6-ナフタレンジカルボン酸ジヒドラジド (0. 084g、0. 344 mmol) 及びテレフタル酸ジヒドラジド (0. 6012g、3. 096mmol)
実施例5	〃	2, 6-ナフタレンジカルボン酸ジヒドラジド (0. 084g、0. 344 mmol) 及び硫酸ヒドラジニウム (0. 4029g、3. 096 mmol)
実施例6	〃	2, 6-ナフタレンジカルボン酸ジヒドラジド (0. 688g、2. 41 mmol) 及び硫酸ヒドラジニウム (0. 134g、1. 03 mmol)
実施例7	1, 1, 3-トリメチル-3-フェニルインダン-4', 5-ジカルボン酸 (0. 895g、2. 75 mmol) 及び 2, 2-ビス(4-カルボキシフェニル)ヘキサフルオロプロパン (0. 27g、0. 69 mmol)	テレフタル酸ジヒドラジド (0. 6679g、3. 44 mmol)
実施例8	1, 1, 3-トリメチル-3-フェニルインダン-4', 5-ジカルボン酸 (1. 0053g、3. 10 mmol) 及びイソフタル酸 (0. 057g、0. 344 mmol)	イソフタル酸ジヒドラジド (0. 6679g、3. 44 mmol)
実施例9	1, 1, 3-トリメチル-3-フェニルインダン-4', 5-ジカルボン酸(1. 117g、3. 44 mmol)	イソフタル酸ジヒドラジド (0. 334g、1. 72 mmol) 及び 2, 6-ナフタレンジカルボン酸ジヒドラジド (0. 42g、1. 72 mmol)
比較例1	1, 1, 3-トリメチル-3-フェニルインダン-4', 5-ジカルボン酸(1. 117g、3. 44 mmol)	硫酸ヒドラジニウム (0. 448g、3. 44mmol)
比較例2	イソフタル酸 (0. 571g、3. 44mmol)	硫酸ヒドラジニウム (0. 448 g、3. 44mmol)

[0100]
[Table 2]

ポリオキサジアゾール誘導体の評価

	ポリオキサジアゾール誘導体	収量(g)	収率(%)	η_{inh} (dl/g)	Tg_5(℃)	Td_5(℃)	ピーク波長λ_{max} (cm^{-1})
実施例1	P1	1. 52	99	0. 39	332	442	383
実施例2	P2	1. 49	98	0. 37	336	443	418
実施例3	P3	1. 38	91	1. 11	318	459	380
実施例4	P4	1. 44	93	0. 32	336	467	422
実施例5	P5	1. 02	91	0. 85	348	465	410
実施例6	P6	1. 43	95	0. 46	355	467	433
実施例7	P7	1. 52	96	0. 33	323	459	419
実施例8	P8	1. 28	95	0. 58	307	467	380
実施例9	P9	1. 46	90	0. 44	334	463	429
比較例1	P10	0. 94	90	0. 28	333	462	381
比較例2	P11	0. 45	90	0. 95	*400	465	380

[0101]
[Table 3]

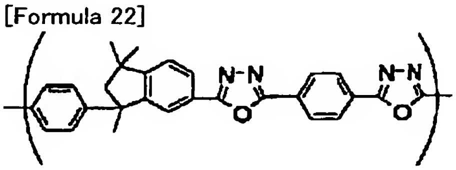
ポリオキサジアゾール誘導体の溶解性

	ポリオキサジアゾール誘導体	1，1，2，2−テトラクロロエタン	クロロホルム	ジクロロメタン	NMP
実施例１	Ｐ１	○	○	○	○
実施例２	Ｐ２	○	×	○	○
実施例３	Ｐ３	○	○	○	○
実施例４	Ｐ４	○	×	△	△
実施例５	Ｐ５	○	○	○	○
実施例６	Ｐ６	○	○	×	○
実施例７	Ｐ７	○	×	△	△
実施例８	Ｐ８	○	○	△	○
実施例９	Ｐ９	○	○	○	○
比較例１	Ｐ１０	×	×	×	×
比較例２	Ｐ１１	×	×	×	×

[0102] (An example 2 - an example 9, and the example 1 of a comparison - the example 2 of a comparison) (Manufacture of a polyoxadiazole derivative) the raw material shown in Table 1 in examples 2-9 — as a dicarboxylic acid component and a dihydrazide component — using it — the same conditions as an example 1, and a procedure — with, the polyoxadiazole derivative (P2-P9) shown in following chemical formula (8) - (15) was manufactured. Moreover, also in the examples 1-2 of a comparison, the raw material shown in Table 1 was used, and the polyoxadiazole derivative (P10-P11) which are the same conditions and a procedure like an example 1, with is shown in chemical formula (16) - (17) was manufactured. In addition, each of a gram (g) unit and a millimol (mmol) unit has shown among the table the amount of the raw material used shown in Table 1.

[0103]

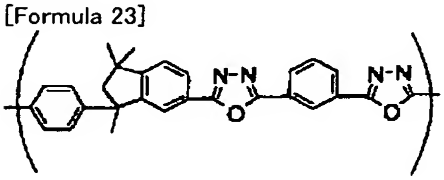
[Formula 22]



(8)

[0104]

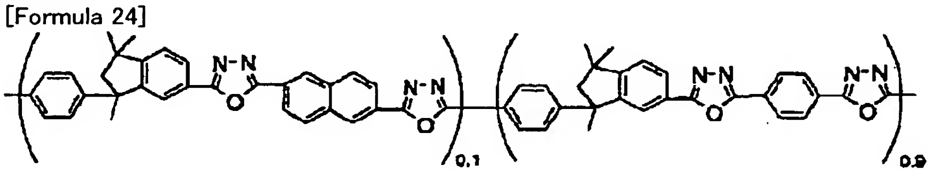
[Formula 23]



(9)

[0105]

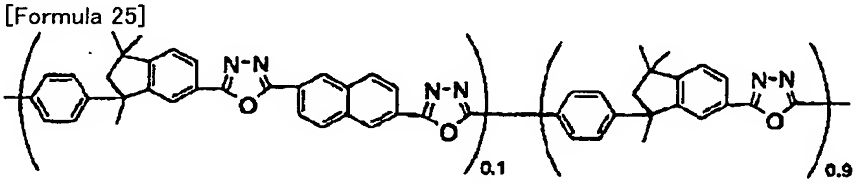
[Formula 24]



(10)

[0106]

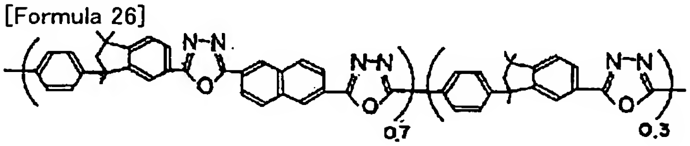
[Formula 25]



(11)

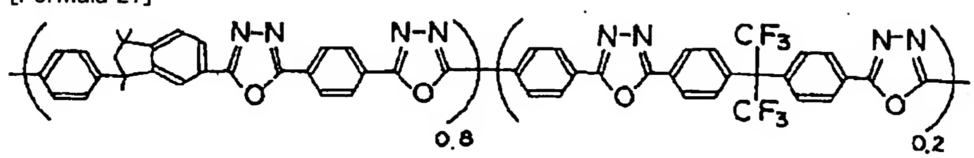
[0107]

[Formula 26]



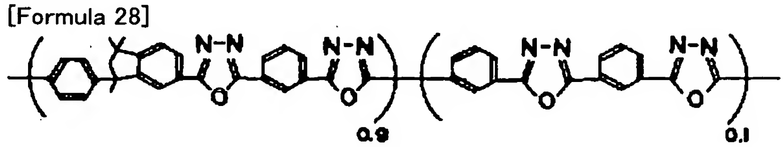
(12)

[0108]
[Formula 27]



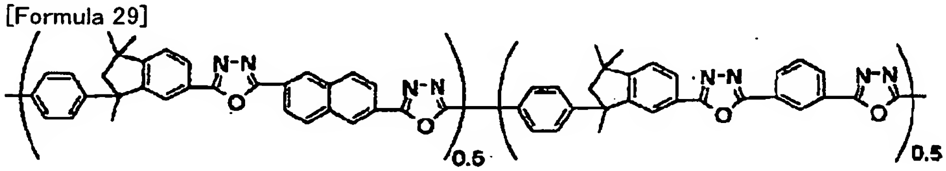
(13)

[0109]
[Formula 28]



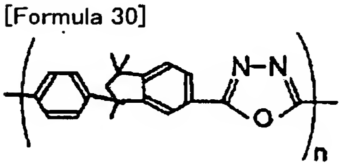
(14)

[0110]
[Formula 29]



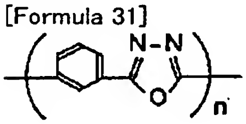
(15)

[0111]
[Formula 30]



(16)

[0112]
[Formula 31]



(17)

[0113] subsequently -- the obtained polyoxadiazole derivative (P2-P11) -- respectively -- an example 1 -- the same -- carrying out -- a logarithm -- viscosity, glass transition temperature, and the decrease pyrolysis temperature of 5% weight were measured. A measurement result is shown in Table 2. In addition, since the obtained polyoxadiazole derivative was crystallizing only the example 2 of a comparison, glass transition temperature was not measured but the melting point was measured instead. Therefore, about the example 2 of a comparison, the value (*400 degree C) of the melting point is shown in the column of Tg among Table 2. Moreover, infrared spectroscopy measurement was performed like the example 1, respectively only about the polyoxadiazole derivative (P2-P9) obtained in the example 2 - the example 9. The chart of the obtained IR spectrum is shown in drawing 2 - drawing 9 , respectively.
[0114] Moreover, about the obtained polyoxadiazole derivative (P2-P11), like the example 1, the fluorescence spectrum (peak wavelength) was measured and the wavelength in the case of emitting light as an organic electroluminescent element was presumed, respectively. Furthermore, about the polyoxadiazole derivative (P10-P11) obtained in the examples 1-2 of a comparison, trifluoroacetic acid was used instead of 1, 1, 2, 2, and - tetrachloroethane, and the fluorescence spectrum (peak wavelength) was measured. The result obtained, respectively is shown in Table 2.
[0115] Moreover, the dissolution sex test to various solvents was performed like the example 1 about the obtained polyoxadiazole derivative (P2-P11), respectively. A result is shown in Table 3.
[0116] (Example 10)
(Creation of an organic electroluminescent element) On the glass substrate with a thickness of 1mm, it is 50nm in thickness, with the indium-tin-oxide compound (ITO) film was formed with the vacuum deposition method. moreover, this ITO film top -- the Pori (p-phenylenevinylene) film of 50nm thickness -- J.Appl.Polym, Sci., and Vol. -- it formed in 26 and 3241 (1988) as an electron hole (hole) transportation layer by the approach of a publication.
[0117] Subsequently, rotation spreading of the solution (10 % of the weight of concentration) made to dissolve the poly oxazole derivative (P2) obtained in the example 2 in 1,1,2,2-tetrachloroethane was carried out on the Pori (p-phenylenevinylene) film using the spin coater. And at the temperature of 80 degrees C, it heat-treated for 2 hours and the poly oxazole derivative film of 50nm thickness was formed as an electronic transportation layer.
[0118] Subsequently, on the obtained poly oxazole derivative film, the vacuum deposition method was used, the

aluminum layer with a thickness of 100nm was formed as cathode in an organic electroluminescent element, and the organic electroluminescent element of this invention was created.

[0119] (Evaluation of an organic electroluminescent element) When the electrical potential difference of 28V was impressed between the ITO electrode of the organic electroluminescent element obtained by doing in this way, and the aluminum electrode, skillful green luminescence was observed. And when measured about the brightness of the luminescence concerned using brightness meter, it is 243 cd/m2. The value to say was acquired.

[0120]

[Effect of the Invention] Common organic solvents, such as 1,1,2,2-tetrachloroethane, can be provided now with a meltable polyoxadiazole derivative by including the OKISA diazole segment which has a phenyl indan radical in intramolecular.

[0121] Moreover, aromatic series dicarboxylic acid dihydrazide, and 1, 1, a 3-trimethyl-3-phenyl indan - 4' and by making 5-dicarboxylic acid react Or aromatic series dicarboxylic acid, and 1, 1, a 3-trimethyl-3-phenyl indan - 4' and by making 5-dicarboxylic acid dihydrazide react The polyoxadiazole derivative containing the OKISA diazole segment which has a phenyl indan radical as it is also at high recovery can be manufactured now.

[0122] Moreover, by using a meltable polyoxadiazole derivative for these common organic solvents, solution spreading was attained and manufacture of an organic electroluminescent element became easy. Furthermore, by solution spreading, since a uniform thin film formed easily, the organic electroluminescent element which was excellent in endurance with high brightness could be offered.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the organic electroluminescent element which used the polyoxadiazole derivative concerned for a polyoxadiazole derivative and its manufacture approach, and a list. It is related with the organic electroluminescent element using the still more nearly meltable polyoxadiazole derivative to the organic solvent concerned about a polyoxadiazole derivative meltable to a more detailed common organic solvent, and its manufacture approach.
[0002]
[Description of the Prior Art] Conventionally, the low-molecular organic compound has been used for the organic electroluminescent element. However, in these components, a low-molecular organic compound may cause degradation to a lifting and a component for crystallization or condensation in connection with the passage of time. If exposed to an elevated temperature by the heat especially generated with a component drive, it will crystallize, therefore component degradation is remarkable. Then, in order to control such component degradation, glass transition temperature is high and using a crystalline low high molecular compound is proposed. Moreover, in order to thin-film-ize a low molecular weight compound, since it is necessary to use means, such as vacuum deposition and the sputtering method, time amount is taken and productivity is bad. On the other hand, a high molecular compound can carry out [thin film]-izing easily by applying a solution. Use of a high molecular compound is called for also from a viewpoint of such a productivity improvement.
[0003] About the electron hole transportation matter, the high molecular compound which was excellent in some is known among the matter which constitutes an organic electroluminescent element. However, about the electronic transportability matter, thing of a certain thing with some sufficient proposals is not yet obtained. the inside of it — 2-(4-biphenylyl)-5-(4-tert-buthylphenyl)- low-molecular OKISA diazole compounds, such as 1, 3, and 4-OKISA diazole (PBT), are known as an ingredient excellent in the electronic transportability in an organic electroluminescent element — **** (Jpn.J.Appl.Phys., 27, L269 (1988)) — some are proposed also about the giant-molecule OKISA diazole compound.
[0004] First, the OKISA diazole compound which has two or more oxadiazole rings in intramolecular is indicated by JP,6-145658,A, JP,6-92947,A, JP,5-152072,A, JP,5-202011,A, and JP,6-136359,A. However, these OKISA diazole compounds of crystallization depressor effect are insufficient, and it gets down also from thin film-ization with vacuum deposition, and the productivity issue is not solved at all.
[0005] Moreover, the OKISA diazole compound which is made to carry out the polymerization of the monomer containing the oxadiazole ring which has the double bond in which a polymerization is possible to an end according to a radical polymerization etc., and is obtained is indicated by JP,8-208745,A and JP,9-255725,A. These OKISA diazole compounds have the oxadiazole ring in the side chain of a giant molecule, and are compounds usable in the electronic transportation layer in an organic electroluminescent element. however, it cannot say that the glass transition temperature of these OKISA diazole compounds is sufficiently high (with a compound given in JP,9-255725,A, it is 179 degrees C), and 10% weight reduction temperature of thermal stability in the inside of nitrogen is inadequate not much highly (**, 394 degrees C) — etc. ７— amelioration of the long term stability of a component is inadequate. Although a high glass transition temperature and thermal stability are expected, since structure becomes upright, generally the polyoxadiazole which repeats and contains an oxadiazole ring in a principal chain cannot melt into an organic solvent easily, and thin-film-izing is difficult for it.
[0006] in order to solve this problem — "— Chem.Mater. — polyoxadiazole is made meltable to an organic solvent by adding a hexafluoro isopropylidene radical to a principal chain, and adding a long-chain alkyl group to a side chain, and closing, if to an organic electroluminescent element is proposed by 1995, 7, and 1568-1575." However, the highest brightness of the organic electroluminescent element using these polyoxadiazole is about 115 cd/m2. It cannot be said with extent that it is not much high. Moreover, although neither glass transition temperature nor weight reduction temperature is indicated, generally, installation of a hexafluoro isopropylidene radical causes the fall of glass transition temperature, and a long-chain alkyl side chain causes not only glass transition temperature but the fall of pyrolysis temperature. Therefore, the viewpoint of the long term stability of a component to these polyoxadiazole is not desirable.
[0007]
[Problem(s) to be Solved] In order to solve the above-mentioned problem, it has the outstanding electronic transport capacity, and it is meltable to an organic solvent, thin-film-izing is easy, and, moreover, development of a

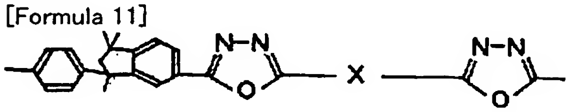
high molecular compound with high thermal stability with high glass transition temperature and pyrolysis temperature has been a technical problem. Then, a header and this invention are completed for having the electronic transport capacity which the artificers of this invention became meltable [polyoxadiazole] to an organic solvent by introducing into intramolecular the OKISA diazole segment which has a phenyl indan radical in a specific joint format as a result of inquiring wholeheartedly, and whose thermal stability was [the polyoxadiazole concerned] high and was moreover excellent.

[0008]

[Means for Solving the Problem] This invention is a polyoxadiazole derivative and is characterized by containing the segment expressed with a general formula (1) to intramolecular.

[0009]

[Formula 11]



(1)

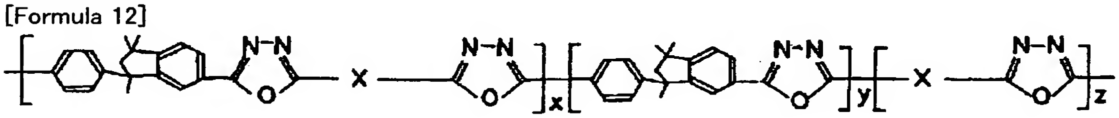
[0010] X is expressed with -Ar-(Z-Ar) n- among [type (1), and Ar shows a divalent aromatic series radical or a divalent heterocycle type aromatic series radical among the X concerned. Z - CRR- or -CR=CR - (R expresses hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, and the aryl group of carbon numbers 6-30.) it is the hydrocarbon group expressed and at least one of O (oxygen atom), S (sulfur atom), and the SO2 (sulfur dioxide), and n is the integer of 0, or 1-2.]

[0011] Thus, by containing in intramolecular the OKISA diazole segment which has a phenyl indan radical in a specific joint format, a meltable polyoxadiazole derivative can be offered to common organic solvents, such as dichloromethane, chloroform, 1,1,2,2-tetrachloroethane, a dichloroethane, or N-methyl pyrrolidone (NMP may be called hereafter).

[0012] Moreover, in constituting a polyoxadiazole derivative, it is desirable that the polyoxadiazole derivative containing the segment expressed with a general formula (1) is the compound (structure) expressed with the following general formula (2).

[0013]

[Formula 12]



(2)

[0014] Among [general formula (2), Ar, Z, and n are the respectively same contents as a general formula (1), the mole ratio of x:y is the value of 100:0-100:1000 within the limits, and the mole ratio of x:z is the value of 100:0-100:500 within the limits.]

[0015] Thus, by constituting a polyoxadiazole derivative, a polyoxadiazole derivative can be more easily dissolved to common organic solvents, such as dichloromethane, 1,1,2,2-tetrachloroethane, etc. which were mentioned above. Therefore, it is at least 1% of the weight or more of concentration, with a polyoxadiazole derivative can be dissolved.

[0016] moreover, a polyoxadiazole derivative -- constituting -- hitting -- the logarithm of the polyoxadiazole derivative concerned -- it is desirable to make viscosity etainh (Measuring condition: the temperature of 30 degrees C, a solvent sulfuric acid, concentration 0.5 g/dl) into the value of 0.1 - 2 dl/g within the limits. such range -- the logarithm of a polyoxadiazole derivative -- viscosity etainh While being able to dissolve the polyoxadiazole derivative concerned in a common organic solvent easily by restricting a value, the uniform thin film excellent in thermal resistance can be formed. Therefore, when the polyoxadiazole derivative concerned is used for the luminous layer in an organic electroluminescent element etc., it excels in endurance, and charge transportability is high and can obtain the organic electroluminescent element of high luminous efficiency.

[0017] Moreover, another mode of this invention is a 1 expressed in following formula (4) as aromatic series dicarboxylic acid dihydrazide which is manufacture approach of polyoxadiazole derivative and is expressed with following general formula (3), 1, and 3-trimethyl-3-phenyl indan. - It is characterized by 4' and making 5-dicarboxylic acid react (the 1st approach).

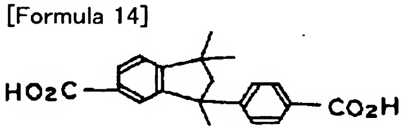
[0018]

[Formula 13]

$$H_2NHNOC-Ar-(Z-Ar)_n-CONHNH_2 \qquad (3)$$

[0019]

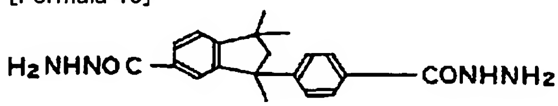
[Formula 14]



(4)

[0020] Ar shows a divalent aromatic series radical or a divalent heterocycle type aromatic series radical among

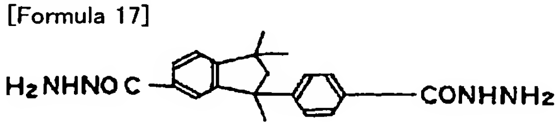
[general formula (3), Z is the hydrocarbon group expressed with -CRR- or -CR=CR- (R expresses hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, or the aryl group of carbon numbers 6-30.), and at least one of O, S, and the SO2, and n is the integer of 0, or 1-2.]
[0021] thus, the thing for which the polyoxadiazole derivative of this invention is manufactured -- a polyoxadiazole derivative meltable to common organic solvents, such as 1,1,2,2-tetrachloroethane, -- being efficient (high recovery) -- it can manufacture.
[0022] Moreover, 1 which is expressed with the following formula (5) in enforcing the manufacture approach (the 1st approach) of the polyoxadiazole derivative in this invention, 1, a 3-trimethyl-3-phenyl indan - It is desirable to make it react including further 4', the aromatic series dicarboxylic acid expressed with 5-dicarboxylic acid dihydrazide and the following general formula (6), or either.
[0023]
[Formula 15]


(5)

[0024]
[Formula 16]

$$HO_2C-Ar\left(-Z-Ar\right)_n-CO_2H \qquad (6)$$

[0025] Ar, Z, and n are the same as that of the contents of said general formula (3) respectively among [general formula (6).]
[0026] thus, the thing for which the polyoxadiazole derivative of this invention is manufactured -- a polyoxadiazole derivative meltable to common organic solvents, such as 1,1,2,2-tetrachloroethane, -- being efficient (high recovery) -- it can manufacture.
[0027] Moreover, another mode of this invention is a 1 which is manufacture approach of polyoxadiazole derivative and is expressed with following formula (5), 1, and 3-trimethyl-3-phenyl indan. - It is characterized by making 4', and 5-dicarboxylic acid dihydrazide and the aromatic series dicarboxylic acid expressed with the following general formula (6) react (the 2nd approach).
[0028]
[Formula 17]


(5)

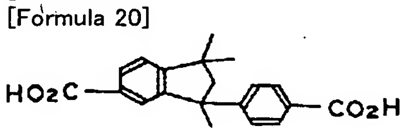
[0029]
[Formula 18]

$$HO_2C-Ar\left(-Z-Ar\right)_n-CO_2H \qquad (6)$$

[0030] Ar, Z, and n are the same as that of the contents of said general formula (3) respectively among [general formula (6).]
[0031] thus, the thing for which the polyoxadiazole derivative of this invention is manufactured -- a polyoxadiazole derivative meltable to common organic solvents, such as 1,1,2,2-tetrachloroethane, -- being efficient (high recovery) -- it can manufacture.
[0032] Moreover, 1 which is expressed with the aromatic series dicarboxylic acid dihydrazide and the following formula (4) which are expressed with the following general formula (3) in enforcing the manufacture approach (the 2nd approach) of the polyoxadiazole derivative in this invention, 1, a 3-trimethyl-3-phenyl indan - It is desirable 4' and to make it react including 5-dicarboxylic acid or either further.
[0033]
[Formula 19]

$$H_2NHNOC-Ar\left(-Z-Ar\right)_n-CONHNH_2 \qquad (3)$$

[0034] Ar, Z, and n are the same as that of the contents mentioned above, respectively among [general formula (3).]
[0035]
[Formula 20]


(4)

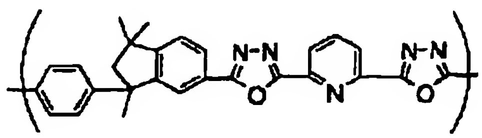
[0036] thus, the thing for which the polyoxadiazole derivative of this invention is manufactured -- a polyoxadiazole derivative meltable to common organic solvents, such as 1,1,2,2-tetrachloroethane, -- being efficient (high recovery) -- it can manufacture.
[0037] Moreover, in enforcing the manufacture approach (the 1st and 2nd approaches) of the polyoxadiazole derivative in this invention, it is desirable to make it react including further hydrazinium sulfate and hydrochloric-acid hydra JINIUMU, or either. Thus, by manufacturing a polyoxadiazole derivative including hydrazinium sulfate or hydrochloric-acid hydra JINIUMU, the content of an OKISA diazole radical can be prepared easily. Therefore, a meltable polyoxadiazole derivative can be manufactured more efficiently (high recovery) quantitatively to common organic solvents, such as 1,1,2,2-tetrachloroethane.
[0038] Moreover, in enforcing the manufacture approach (the 1st and 2nd approaches) of the polyoxadiazole derivative in this invention, it is desirable to be each total amount, with to be the mole ratio of 40:60-60:40 (dihydrazide component: dicarboxylic acid component) within the limits, and to make a dihydrazide component and a dicarboxylic acid component react especially by the mole ratio of 45:55-55:45 (dihydrazide component: dicarboxylic acid component) within the limits. In addition, a dihydrazide component shows the compound expressed with a general formula (3), the compound expressed with a general formula (5), hydrochloric-acid hydra JINIUMU, and hydrazinium sulfate. Moreover, a dicarboxylic acid component shows the compound, hydrochloric-acid hydra JINIUMU, and hydrazinium sulfate which are expressed with a general formula (4) and a general formula (5).
[0039] moreover, another mode of this invention is characterized by two or more organic layers containing a luminous layer or a luminous layer concerned being further alike at least, and containing the polyoxadiazole derivative mentioned above in the organic electroluminescent element equipped with two or more organic layers which contain a luminous layer or a luminous layer in inter-electrode [of a pair].
[0040] By having the outstanding charge transportability, therefore constituting an organic electroluminescent element in this way, the polyoxadiazole derivative mentioned above can demonstrate the outstanding charge transportability, and can offer an organic electroluminescent element with a quick speed of response.
[0041] Moreover, since it can be made to dissolve in common organic solvents, such as 1,1,2,2-tetrachloroethane, easily, when producing an organic electroluminescent element, the polyoxadiazole derivative of this invention is easy handling, and it can use it as a uniform thin film.
[0042] Furthermore, in constituting the organic electroluminescent element of this invention, it is desirable to contain the polyoxadiazole derivative of this invention which used one of the organic layers as the charge transportation layer (electronic transportation layer), and was mentioned above in the charge transportation layer (electronic transportation layer) concerned. Thus, by constituting an organic electroluminescent element, the outstanding charge transportability (electronic transportability) which the polyoxadiazole derivative of this invention has can be demonstrated more efficiently, and the organic electroluminescent element of high luminous efficiency can be offered.
[0043]
[Embodiment of the Invention] Hereafter, the operation gestalten 1-3 of this invention are explained more concretely. First, the 1st operation gestalt of this invention is a polyoxadiazole derivative, and is characterized by including the OKISA diazole segment which is expressed with said general formula (1) and which has a phenyl indan radical.
[0044] Moreover, in order to acquire the fusibility over a higher organic solvent, it is desirable that the OKISA diazole segment which does not have the segment and phenyl indan radical which the phenyl indan radical and the oxadiazole ring coupled directly is included in intramolecular random or in the shape of a block with the OKISA diazole segment which has a phenyl indan radical so that it may be expressed with said general formula (2).
[0045] However, the OKISA diazole segment which does not have the segment and phenyl indan radical which the phenyl indan radical and the oxadiazole ring coupled directly is easy to contain either, respectively. In that case, when [of the OKISA diazole segment which has a phenyl indan radical] (x) is comparatively made into 100 mols, it is desirable to make [of the OKISA diazole segment in which making / of the segment which the phenyl indan radical and the oxadiazole ring coupled directly / (y) into the value within the limits of 0-1000 mols comparatively does not have a phenyl indan radical similarly preferably] (z) into the value within the limits of 0-500 mols comparatively.
[0046] Making Ar into the aromatic series radical of bivalence or the heterocycle type aromatic series radical of bivalence among a general formula (1) and a general formula (2) here has good reactivity if it is these radicals, when manufacturing a polyoxadiazole derivative, and it is because it can consider as the thin film of the polyoxadiazole derivative which raised the glass transition temperature of the polyoxadiazole derivative obtained, and was excellent in endurance or thermal resistance.
[0047] Moreover, they are the inside of a general formula (1) and a general formula (2), and Z -CRR- or -CR=CR - (R) hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, or the aryl group of carbon numbers 6-30 is expressed. A hydrocarbon group, and O, S and SO2 which are expressed If it is these radicals, it will be referred to as at least one because reactivity when manufacturing a polyoxadiazole derivative is good.
[0048] Furthermore, with [reactivity / reactivity if it is this integer, when manufacturing a polyoxadiazole derivative is good, and] such a raw material, the several n repeat in a general formula (1) and a general formula (2) is made into the integer of 0, or 1-2 because it is easily available.

[0049] Furthermore, if it is the value of this within the limits, make the mole ratio of x:y into the value of 100:0-100:1000 within the limits among a general formula (2), and because the obtained OKISA diazole derivative becomes meltable to an organic solvent, let the mole ratio of x:z be the value of 100:0-100:500 within the limits.
[0050] Moreover, in the polyoxadiazole derivative of this invention, it is desirable to make glass transition temperature (Tg) of the polyoxadiazole derivative concerned into the value of 200 degrees C or more. Thus, by controlling the value of glass transition temperature (Tg) and constituting a polyoxadiazole derivative, it is because it excels in thermal resistance etc. and a possibility of crystalizing can obtain the polyoxadiazole derivative of few thin films. And the glass transition temperature (Tg) of a more desirable polyoxadiazole derivative is 250 degrees C or more in value, and is 300 degrees C or more in value the optimal. In addition, the glass transition temperature (Tg) of the polyoxadiazole derivative concerned can be measured in a nitrogen air current using DSC (Differential Scanning Calorimeter).
[0051] Moreover, in the polyoxadiazole derivative of this invention, it is desirable to make decrease pyrolysis temperature of 5% weight of the polyoxadiazole derivative concerned (Td5) into the value of 200 degrees C or more from a viewpoint which can obtain the polyoxadiazole derivative excellent in thermal resistance, endurance, etc. And the more desirable decrease pyrolysis temperature of 5% weight of a polyoxadiazole derivative (Td5) is 250 degrees C or more in value, and is 300 degrees C or more in value the optimal. In addition, the decrease pyrolysis temperature of 5% weight of the polyoxadiazole derivative concerned (Td5) can be measured, using TGA (Thermal GravityAnalyzer) as temperature at the time of weight decreasing 5% from an initial mass.
[0052] moreover, molecular weight although it has sufficient thermal resistance and endurance even if the end closure of the polyoxadiazole derivative of this invention is not carried out, in order that it may raise thermal resistance and endurance further — adjusting — a suitable logarithm — in order to consider as viscosity, end encapsulant may be used and end closure of the end of a polyoxadiazole derivative derivative may be carried out.
[0053] Here, as usable end encapsulant, kinds, such as hydrazides of aromatic series monocarboxylic acid, such as a benzoic acid, 1-naphthoic acid, 2-naphthoic acid, 4-biphenyl carboxylic acid, and 2-pyridinecarboxylic acid, or these aromatic series monocarboxylic acid, or two sorts or more are mentioned. And it is desirable to make the amount of this end encapsulant used into the value within the limits of 0.001-0.25 mols per one mol of polyoxadiazole derivatives.
[0054] moreover, the logarithm of the viewpoint which is excellent in thermal resistance and can be used as a uniform thin film in the polyoxadiazole derivative of this invention while being able to make it dissolve in a common organic solvent easily to a polyoxadiazole derivative -- it is desirable to make viscosity etainh (Measuring condition: the temperature of 30 degrees C, a solvent sulfuric acid, concentration 0.5 g/dl) into the value of 0.1 - 2.0 dl/g within the limits.
[0055] and the logarithm of a viewpoint with the better balance of the solubility over an organic solvent, and thermal resistance and uniform film production nature to a polyoxadiazole derivative — viscosity etainh It is considering as the value of 0.6 - 1.2 dl/g within the limits more preferably [considering as the value of 0.5 - 1.5 dl/g within the limits], and the optimal.
[0056] Next, the 2nd operation gestalt of this invention is explained. The aromatic series dicarboxylic acid dihydrazide which this 2nd operation gestalt is the efficient manufacture approach of a polyoxadiazole derivative, and is expressed with said general formula (3), 1 expressed with said general formula (4), 1, 3-trimethyl-3-phenyl indan - (the 1st approach) [4' and] [whether 5-dicarboxylic acid is made to react and] Or 1 expressed in said formula (6) as the aromatic series dicarboxylic acid expressed with said general formula (5), 1, a 3-trimethyl-3-phenyl indan - It is characterized by 4' and the thing which you make 5-dicarboxylic acid dihydrazide react (the 2nd approach).
[0057] Here, it is -CRR about the reason and Z which make Ar the aromatic hydrocarbon radical of bivalence, or the heterocycle type aromatic series radical of bivalence among a general formula (3) and a general formula (5). - (R) hydrogen, the alkyl group of carbon numbers 1-6, the alkyl halide radical of carbon numbers 1-6, and the aryl group of carbon numbers 6-30 are expressed. A hydrocarbon group, and O, S and SO2 which are expressed The reason for making into the integer of 0, or 1-2 the reason set to at least one and a several n repeat is the same as the reason explained by the general formula (1) and the general formula (2), respectively.
[0058] moreover, in enforcing the manufacture approach (the 1st approach) of the polyoxadiazole derivative in this invention, as aromatic series dicarboxylic acid dihydrazide expressed with a general formula (3) Phthalic-acid dihydrazide, terephthalic-acid dihydrazide, isophthalic acid dihydrazide, 1, 4-naphthalene dicarboxylic acid dihydrazide, 2, 3-naphthalene dicarboxylic acid dihydrazide, 2, 6-naphthalene dicarboxylic acid dihydrazide, 2, 3-pyridine dicarboxylic acid dihydrazide, 2, 4-pyridine dicarboxylic acid dihydrazide, 2, 5-pyridine dicarboxylic acid dihydrazide, 2,6-pyridine-dicarboxylic-acid dihydrazide, 3, 5-pyridine dicarboxylic acid dihydrazide, - biphenyl dicarboxylic acid dihydrazide, and 2 and 2 '4, 4'-biphenyl dicarboxylic acid dihydrazide, 9-full -- me -- non -2, 7-dicarboxylic acid dihydrazide, a stilbene -4, and 4'-dicarboxylic acid dihydrazide -- - JIHIDORAJINO carbonyl diphenyl ether, and 4 and 4 '4, 4'-JIHIDORAJINO carbonyl diphenylsulfone, A 4 and 4'-JIHIDORAJINO carbonyl diphenyl sulfide, It is desirable to use at least one aromatic series dicarboxylic acid dihydrazide chosen from the group which consists of a 2 and 2-screw (4-hydrazino carbonyl phenyl) hexafluoropropane and 2, and 2-screw (4-hydrazino carbonyl phenyl) propane. These aromatic series dicarboxylic acid dihydrazide is a 1, 1, and 3-trimethyl-3-phenyl indan. - Reactivity with 4' and 5-dicarboxylic acid is good, and recovery high about a polyoxadiazole derivative is acquired, and acquisition is also because it is easy.
[0059] Moreover, 1 which is expressed in a formula (4) as the aromatic series dicarboxylic acid dihydrazide

expressed with a general formula (3) in enforcing the manufacture approach (the 1st approach) of the polyoxadiazole derivative in this invention, 1, a 3-trimethyl-3-phenyl indan - In making 5-dicarboxylic acid react, it is desirable 4' and to make the reaction mole ratio concerned into the value of 40:60-60:40 within the limits. By making a reaction mole ratio into the value of this within the limits, it is for the reaction at the time of manufacturing about [that the obtained OKISA diazole derivative becomes meltable to an organic solvent certainly] and an OKISA diazole derivative to arise certainly, and for the amount of unreacted components to decrease.
[0060] Therefore, 1 expressed in a formula (4) as the aromatic series dicarboxylic acid dihydrazide expressed with the general formula (3) which hits enforcing the 1st approach, 1, a 3-trimethyl-3-phenyl indan - More preferably, the reaction mole ratio with 5-dicarboxylic acid is the value of 45:55-55:45 within the limits, and are 4' and considering as the value of 48:52-52:48 within the limits the optimal.
[0061] moreover, in enforcing the manufacture approach (the 2nd approach) of the polyoxadiazole derivative in this invention, as aromatic series dicarboxylic acid expressed with a general formula (5) A phthalic acid, a terephthalic acid, isophthalic acid, 1, 4-naphthalene dicarboxylic acid, 2, 3-naphthalene dicarboxylic acid, 2, 6-naphthalene dicarboxylic acid, 2, 3-pyridine dicarboxylic acid, 2, 4-pyridine dicarboxylic acid, 2, 5-pyridine dicarboxylic acid, 2,6-pyridine-dicarboxylic-acid, 3, 5-pyridine dicarboxylic acid, 4, and 4'-biphenyl dicarboxylic acid, 2 and 2'-biphenyl dicarboxylic acid and 9-full -- me -- non -2 and 7-dicarboxylic acid -- A stilbene -4, - dicarboxylic acid, and 4 '4, 4'-dicarboxy diphenyl ether, A - dicarboxy diphenylsulfone, and 4 and 4 '4, 4'-dicarboxy diphenyl sulfide, It is desirable to use at least one aromatic series dicarboxylic acid chosen from the group which consists of a 2 and 2-screw (4-carboxyphenyl) hexafluoropropane and 2, and 2-screw (4-carboxyphenyl) propane. These aromatic series dicarboxylic acid is a 1, 1, and 3-trimethyl-3-phenyl indan. - Reactivity with 4', 5-dicarboxylic acid dihydrazide, etc. is good, and recovery high about a polyoxadiazole derivative is acquired, and the acquisition itself is because it is easy.
[0062] Moreover, 1 which is expressed in a formula (6) as the aromatic series dicarboxylic acid expressed with a general formula (5) in enforcing the manufacture approach (the 2nd approach) of the polyoxadiazole derivative in this invention, 1, a 3-trimethyl-3-phenyl indan - It is desirable 4' and to make a reaction mole ratio with 5-dicarboxylic acid dihydrazide into the value of 40:60-60:40 within the limits. By making a reaction mole ratio into the value of this within the limits, it is for the reaction at the time of manufacturing about [that the obtained OKISA diazole derivative becomes meltable to an organic solvent certainly] and an OKISA diazole derivative to arise certainly, and for the amount of unreacted components to decrease.
[0063] Therefore, 1 which is expressed in a formula (6) as the aromatic series dicarboxylic acid expressed with a general formula (5) in enforcing the 2nd approach, 1, a 3-trimethyl-3-phenyl indan - It is 4' and being the value of 45:55-55:45 within the limits, and making more preferably, a reaction mole ratio with 5-dicarboxylic acid dihydrazide into the value of 48:52-52:48 within the limits the optimal. In addition, in the manufacture approach of this invention, when calling it the amount of a dicarboxylic acid component and the dihydrazide component used, the total amount of a dicarboxylic acid component and the total amount of a dihydrazide component are said, respectively. Moreover, when hydrazinium sulfate and hydrochloric-acid hydra JINIUMU are used, these hydra JINIUMU is converted as a dihydrazide component.
[0064] Moreover, in enforcing the manufacture approach (the 1st and 2nd approaches) which is the 2nd operation gestalt of this invention, it is desirable to use a condensing agent. Namely, the aromatic series dicarboxylic acid dihydrazide expressed with said general formula (3), 1 expressed with said formula (4), 1, 3-trimethyl-3-phenyl indan - (the 1st approach) [4' and] [whether 5-dicarboxylic acid is made to react under existence of a condensing agent, and] Or 1 expressed in said formula (6) as the aromatic series dicarboxylic acid expressed with said general formula (5), 1, a 3-trimethyl-3-phenyl indan - 4' and the thing which you make 5-dicarboxylic acid dihydrazide react under existence of a condensing agent (the 2nd approach) are desirable. Thus, by using a condensing agent, a polyoxadiazole derivative can be manufactured more efficiently (high recovery) quantitatively.
[0065] Here, the class of condensing agent to be used cannot be asked, for example, can use Pori phosphoric acid etc. Moreover, it is more desirable to use the mixture of 5 oxidation **** and methansulfonic acid as a condensing agent from a viewpoint which can produce the reaction of hydrazide and a carboxylic acid alternative moreover very efficiently.
[0066] and the case where the mixture of 5 oxidation **** and methansulfonic acid is used -- the mixing ratio of the 5 oxidation **** concerned and methansulfonic acid -- although especially a rate is not asked, either, it is desirable to make methansulfonic acid into the value of the 300 - 3000 weight section within the limits to the 5 oxidation **** 100 weight section from a viewpoint in which the more excellent condensation effectiveness can be demonstrated and an excessive condensing agent does not remain. And it is desirable to heat the mixture of 5 oxidation **** and methansulfonic acid beforehand in a 50-150-degree C temperature requirement, and to dissolve 5 oxidation **** into methansulfonic acid from a viewpoint which can demonstrate the further excellent condensation effectiveness.
[0067] Moreover, in enforcing the manufacture approach (the 1st and 2nd approaches) of this invention, reaction temperature is made into the value within the limits of 50-150 degrees C from a viewpoint which can manufacture the polyoxadiazole derivative of this invention more efficiently and certainly, and it is desirable to carry out a condensation reaction for 2 to 72 hours. And more preferably, reaction temperature is made into the value within the limits of 80-120 degrees C, and it is the thing for 5 to 72 hours to do for a condensation reaction.
[0068] Finally, the 3rd operation gestalt of this invention is explained. this 3rd operation gestalt is the organic electroluminescent element which used the polyoxadiazole derivative, and is characterized by having two or more

organic layers which contain a luminous layer or a luminous layer in inter-electrode [of a pair], and for two or more organic layers containing a luminous layer or a luminous layer concerned being further alike at least, and containing the polyoxadiazole derivative mentioned above.
[0069] Here, various kinds of modes can be taken as a configuration of an organic electroluminescent element. For example, the configuration which formed the luminous layer in inter-electrode [of a pair] (an anode plate and cathode), the configuration which formed the luminous layer and the electron hole (hole) transportation layer in inter-electrode [of a pair] (an anode plate and cathode), The configuration which formed the luminous layer and the electronic (electron) transportation layer in inter-electrode [of a pair] (an anode plate and cathode), It can consider as the configuration which formed the electron hole transportation layer, the luminous layer, and the electronic transportation layer in inter-electrode [of a pair] (an anode plate and cathode), or the configuration which formed the electron injection layer and the hole-injection layer in contact with the electrode further. Namely, what is necessary is just the configuration of the organic electroluminescent element equipped with two or more organic layers which contain a luminous layer or a luminous layer in inter-electrode [of a pair].
[0070] In addition, it is also possible to form a glass substrate and a plastics base material in a lower part (inferior surface of tongue) side as a supporting material of the component in these organic electroluminescent elements if needed.
[0071] And the case where a luminous layer is formed in inter-electrode [of a pair] (an anode plate and cathode) among the configurations in these organic electroluminescent elements is concretely explained using drawing 1 .
[0072] The laminating of the organic electroluminescent element 10 in drawing 1 is carried out, and the order of a glass substrate 1, the ITO film (anode plate) 2, the luminous layer 3 containing a polyoxadiazole derivative, and the aluminum layer (cathode) 4 constitutes it from the lower part. This organic electroluminescent element 10 is electrically connected to external DC power supply 5 through the ITO film (anode plate) 2 vapor-deposited and formed on the glass substrate 1, and the aluminum layer (cathode) 4 which similarly vapor-deposited and was formed.
[0073] Therefore, if an electrical potential difference is impressed from external DC power supply 5, an electron will be poured in from the aluminum layer (cathode) 4, and this electron will be sent to a luminous layer 3. On the other hand, if an electrical potential difference is impressed from DC power supply 5, an electron hole (hole) will be poured in from the ITO film (anode plate) 2, and this electron hole will be sent to a luminous layer 3. That is, in a luminous layer 3, an electron and an electron hole recombine and recombination energy is emitted. Therefore, this recombination energy will be emitted as an electroluminescence light.
[0074] In addition, in order to use the recombination energy of this electron and electron hole more efficiently, it is also possible to include photogene in a luminous layer 3, to excite photogene with the recombination energy concerned, and to emit light as electroluminescence.
[0075] Moreover, although especially the thickness of two or more organic layers (for example, electron hole transportation layer) containing a luminous layer 3 or a luminous layer is not restricted, it is considering as the value within the limits of 10nm - 200nm preferably [usually making thickness per layer into the value within the limits of 1nm - 1000nm], and more preferably.
[0076] In addition, since it is possible to apply the polyoxadiazole derivative of the amount of giant molecules concerned using the organic solvent of a low-boiling point when forming the polyoxadiazole derivative of this invention as one of two or more of the organic layers containing a luminous layer or a luminous layer, a uniform thin film can be formed rather than there are few defects of a pinhole etc.
[0077] Moreover, as an ingredient of the anode plate 2 in the organic electroluminescent element 10 with which it was expressed to drawing 1 , although the indium-tin-oxide compound (ITO) is used, if it is a large (4eV or more as an example) metal, an alloy or an oxide conductor of a work function, etc., it is usable. And as a concrete ingredient, the use of transparence oxide conductors, such as alloys, such as metals, such as Au, and Au/nickel, or a diacidized tin compound (SnO_2), and a zinc oxide (ZnO), other than the indium-tin-oxide compound (ITO) mentioned above is desirable.
[0078] Moreover, since taking out luminescence from the anode plate side of an organic electroluminescent element generally is performed, as an ingredient of the anode plate concerned, a transparent electrode ingredient is desirable, therefore it is optimal to use the transparence oxide conductor mentioned above as an anode material.
[0079] In addition, it will go caudad, electroluminescence light will be emitted and it enables it to have taken out electroluminescence light outside through the ITO film 2 and a glass substrate 1 in the organic electroluminescent element 10 of a configuration of being shown in drawing 1 .
[0080] moreover -- although especially the thickness of an anode plate is not what is limited -- from a viewpoint with the good balance of transparency and membranous homogeneity -- usually -- the range of 10-1000nm -- it is more preferably chosen within the limits of 10-200nm. Furthermore, although especially the process of an anode plate is not limited, either, it can form by the general technique, such as vacuum evaporationo and sputtering.
[0081] As an ingredient of the cathode 4 in the organic electroluminescent element 10 with which it was expressed to drawing 1 on the other hand, a small (less than 4eV as an example) metal, an alloy or a conductive compound of a work function, etc. is desirable. Although aluminum is used in this example, it is also desirable to use alloys, such as metals, such as calcium, magnesium, a lithium, and an indium, an aluminium alloy, a calcium alloy, a Magnesium alloy, and a lithium alloy.
[0082] in addition -- although it is not what is especially limited also about the thickness of cathode -- from a viewpoint with the good balance of internal resistance and membranous homogeneity -- usually -- the range of 10-

1000nm -- it is more preferably chosen within the limits of 50-200nm. Moreover, although especially the process of cathode is not limited, either, it can form by the general technique, such as vacuum evaporationo and sputtering, like an anode plate.
[0083] Moreover, in constituting the organic electroluminescent element 10 mentioned above, as mentioned above, it is desirable to contain the polyoxadiazole derivative of this invention in a luminous layer 3 (for it to be an electronic transportation layer separately, when the electronic transportation layer is prepared) from a viewpoint which can be made to be able to demonstrate more efficiently the outstanding electronic transportability which a polyoxadiazole derivative has, and can offer an organic electroluminescent element with a speed of response quick further more.
[0084] And preferably [considering as at least 10 % of the weight or more] as a content of a polyoxadiazole derivative, and more preferably, it is 50 % of the weight or more, and is 90% of the weight or more of a value the optimal. When the content of a polyoxadiazole derivative becomes less than 10 % of the weight, it is because there is a possibility that electronic transportability may fall remarkably.
[0085] In addition, the polymeric materials for raising film production nature besides the luminescent material mentioned later as ingredients other than the polyoxadiazole derivative in a luminous layer 3, the compound which has one or more oxadiazole rings in which structure differs from the polyoxadiazole derivative of this invention for raising electronic transportability more, a diphenyl quinone derivative and a thiophene derivative, a triazole derivative, a thiadiazole derivative, a quinoxaline derivative, a phenanthroline derivative, etc. are mentioned.
[0086] In constituting the organic electroluminescent element 10 mentioned above moreover, in the electron hole transportation layer 2 A polyvinyl carbazole (PVCZ), N-phenyl carbazole, Pori (p-phenylenevinylene), N, N'-diphenyl-N, N'-JI (3-methylphenyl) -4, a 4'-diamino biphenyl (TPD), One, such as 1 and 1-screw (4-G p-tolylamino phenyl) cyclohexane, N, N'-diphenyl-N, N'-dinaphthyl -4, a 4'-diamino biphenyl, a phthalocyanine derivative, and polysilane, or two or more are usable.
[0087] Moreover, in constituting the organic electroluminescent element 10 mentioned above, as a luminescent material in a luminous layer 3, can use well-known ingredients, such as a daylight fluorescence ingredient, a fluorescent brightener, laser coloring matter, and an organic scintillator, but More specifically An anthracene, a phenanthrene, a pyrene, a chrysene, Perylene, coronene, rubrene, Quinacridone, quarter phenyl, 1, 4-screw (2-methyl styryl) benzene, 1, 4-screw (4-methyl styryl) benzene, One or two compounds or more, such as 1, 4-screw (4-methyl-5-phenyl-2-oxazolyl) benzene, 2, 5-screw (5-tertiary butyl-2-benzoxazolyl) thiophene, 1, 4-diphenyl-1,3-butadiene, and a metal complex, are mentioned.
[0088] Although the configuration (organic electroluminescent element) of the 3rd operation gestalt [in / the above passage / this invention] was explained about the case where a luminous layer is formed in inter-electrode [of a pair] (an anode plate and cathode), using drawing 1 as an example The configuration which formed the luminous layer and the electron hole (hole) transportation layer in inter-electrode [of a pair] (an anode plate and cathode), The same ingredient and the thickness range are employable with having already explained to inter-electrode [of the configuration which formed the luminous layer and the electronic (electron) transportation layer in inter-electrode / of a pair / (an anode plate and cathode), and a pair] (an anode plate and cathode) also in the configuration in which the electron hole transportation layer, the luminous layer, and the electronic transportation layer were formed etc.
[0089]
[Example] Hereafter, this invention is more concretely explained based on an example. However, although it is needless to say, the following publications do not explain this invention generally and this invention is not limited by this publication without a special reason.
[0090] (Example 1)
(Manufacture of a polyoxadiazole derivative) It heated at 100 degrees C, having held 22ml methansulfonic acid and 3.6g 5 oxidation **** in 100ml flask, and agitating the inside of a flask in it using a stirrer. And 5 oxidation **** was dissolved to methansulfonic acid, and it considered as the condensing agent solution. Next, to this condensing agent solution, a mole ratio 1:1 comes out comparatively, with it is a 1.117g (3.44mmol) 1, 1, and 3-trimethyl-3-phenyl indan. - 4', 5-dicarboxylic acid, and 0.6714g (3.44mmol) 2,6-pyridine-dicarboxylic-acid dihydrazide were added.
[0091] And agitating the inside of a flask using a stirrer, at the temperature of 120 degrees C, the condensation reaction was performed about these reaction raw materials, and reaction mixture was obtained for 11 hours. Next, after cooling the temperature in a flask to a room temperature, underwater [in a beaker / about 300ml] was filled with the obtained reaction mixture, and the powdery solid-state product was deposited. And the obtained solid-state product was carried out the ** exception using the filter paper, it is water, a sodium-hydrogencarbonate water solution, water, and a methanol, with sequential washing was carried out. Then, the vacuum drying of the obtained solid-state product was carried out.
[0092] Consequently, the weight of the obtained solid-state product (P1 may be called hereafter) was 1.52g, and recovery was very as high as 99%. Moreover, when infrared spectroscopy measurement was performed to the obtained solid-state product, the wave numbers 2956, 1612, and 1577 and a peak characteristic of 1544cm-1 were acquired, and it was checked that the polyoxadiazole derivative shown in a bottom type (7) is manufactured. In addition, the IR spectrum measured to drawing 1 is shown. This IR spectrum takes the wave number (cm-1) on an axis of abscissa, is shown on it, takes permeability (%) on an axis of ordinate, and is shown on it.
[0093]
[Formula 21]



(7)

[0094] moreover, the logarithm of the obtained polyoxadiazole derivative -- when viscosity etainh (Measuring condition: the temperature of 30 degrees C, a solvent sulfuric acid, concentration of 0.5g / dl) was measured, the value of 0.39 dl/g was acquired. Moreover, when the glass transition temperature (Measuring condition: programming-rate 10degree C/min., nitrogen air current) of the obtained polyoxadiazole derivative was measured using DSC, the high value of 332 degrees C was acquired. Furthermore, when the decrease pyrolysis temperature of 5% weight of the obtained polyoxadiazole derivative (Measuring condition: programming-rate 10degree C/min.) was measured using TGA, the high value of 442 degrees C was acquired.
[0095] (Preparation of a polyoxadiazole derivative solution) About the obtained solid-state product, the dissolution sex test to various solvents was performed, preparing a polyoxadiazole derivative solution. That is, to 1,1,2,2-tetrachloroethane, chloroform, dichloromethane, and NMP, when [of a room temperature (25 degrees C) and 1 - 5 % of the weight of concentration] it came out comparatively, with was made to dissolve, the transparent polyoxadiazole derivative solution was able to be altogether prepared for the polyoxadiazole derivative. A result is shown in Table 3.
[0096] In addition, O mark in Table 3 shows the case of 5 % of the weight of concentration where it was able to come out comparatively, with a transparent polyoxadiazole derivative solution is able to be prepared, it comes out comparatively, with ** mark shows the case of 5 % of the weight of concentration where a polyoxadiazole derivative solution is able to be prepared, although it is opaque a part, and even if x mark is the rate of 1 % of the weight of concentration, it shows the case where a polyoxadiazole derivative solution is not able to be dissolved. Hereafter, the same decision criterion estimated solubility.
[0097] Therefore, the obtained polyoxadiazole derivatives are 1,1,2,2-tetrachloroethane, chloroform, dichloromethane, and the common organic solvent of NMP, and it was checked that the solubility (fusibility may be called) which was excellent to the organic solvent of a low-boiling point is shown so that I might be easily understood from the result of Table 3.
[0098] (Measurement of a fluorescence spectrum) Using the 1,1,2,2-tetrachloroethane solution (10 % of the weight of concentration) of a polyoxadiazole derivative, it is the cast method, with the thin film with a thickness of 20 micrometers was formed on the glass plate. And blue fluorescence was emitted when ultraviolet rays were irradiated to the thin film of the polyoxadiazole derivative which carried out in this way and was formed. And when the fluorescence spectrum was measured, it is peak wavelength lambdamax. It carried out and the value of 383nm was acquired. Therefore, when the thin film of the polyoxadiazole derivative concerned is used for the luminous layer of an organic electroluminescent element, emitting light near 383nm is presumed.
[0099]
[Table 1]

ポリオキサジアゾール誘導体の製造

	ジカルボン酸(使用量)	ジヒドラジド化合物(使用量)
実施例1	1,1,3-トリメチル-3-フェニルインダン-4',5-ジカルボン酸(1.117g、3.44 mmol)	2,6-ピリジンジカルボン酸ジヒドラジド (0.6714g、3.44mmol)
実施例2	〃	テレフタル酸ジヒドラジド (0.6679g、3.44 mmol)
実施例3	〃	イソフタル酸ジヒドラジド (0.6679g、3.44 mmol)
実施例4	〃	2,6-ナフタレンジカルボン酸ジヒドラジド(0.084g、0.344 mmol)及びテレフタル酸ジヒドラジド(0.6012g、3.096mmol)
実施例5	〃	2,6-ナフタレンジカルボン酸ジヒドラジド(0.084g、0.344 mmol)及び硫酸ヒドラジニウム (0.4029g、3.096 mmol)
実施例6	〃	2,6-ナフタレンジカルボン酸ジヒドラジド(0.588g、2.41 mmol)及び硫酸ヒドラジニウム (0.134g、1.03 mmol)
実施例7	1,1,3-トリメチル-3-フェニルインダン-4',5-ジカルボン酸(0.895g、2.75 mmol)及び 2,2-ビス(4-カルボキシフェニル)ヘキサフルオロプロパン(0.27g、0.69 mmol)	テレフタル酸ジヒドラジド (0.6679g、3.44 mmol)
実施例8	1,1,3-トリメチル-3-フェニルインダン-4',5-ジカルボン酸(1.0053g、3.10 mmol)及びイソフタル酸 (0.057g、0.344 mmol)	イソフタル酸ジヒドラジド (0.6679g、3.44 mmol)
実施例9	1,1,3-トリメチル-3-フェニルインダン-4',5-ジカルボン酸(1.117g、3.44 mmol)	イソフタル酸ジヒドラジド (0.334g、1.72 mmol) 及び2,6-ナフタレンジカルボン酸ジヒドラジド(0.42g、1.72 mmol)
比較例1	1,1,3-トリメチル-3-フェニルインダン-4',5-ジカルボン酸(1.117g、3.44 mmol)	硫酸ヒドラジニウム (0.448g、3.44mmol)
比較例2	イソフタル酸 (0.571g、3.44mmol)	硫酸ヒドラジニウム (0.448 g、3.44mmol)

[0100]
[Table 2]

ポリオキサジアゾール誘導体の評価

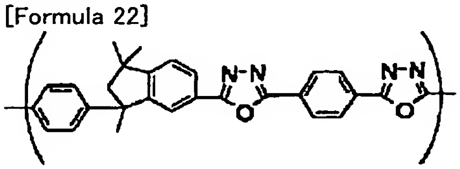
	ポリオキサジアゾール誘導体	収量(g)	収率(%)	η_{inh} (dl/g)	Tg_{s}(℃)	Td_{5}(℃)	ピーク波長λ_{max} (cm^{-1})
実施例1	P1	1.52	99	0.39	332	442	383
実施例2	P2	1.49	98	0.37	336	443	418
実施例3	P3	1.38	91	1.11	318	459	380
実施例4	P4	1.44	93	0.32	336	467	422
実施例5	P5	1.02	91	0.85	348	465	410
実施例6	P6	1.43	95	0.46	355	467	433
実施例7	P7	1.52	96	0.33	323	459	419
実施例8	P8	1.28	95	0.58	307	467	380
実施例9	P9	1.46	90	0.44	334	463	429
比較例1	P10	0.94	90	0.28	333	462	381
比較例2	P11	0.45	90	0.95	*400	465	380

[0101]
[Table 3]

ポリオキサジアゾール誘導体の溶解性

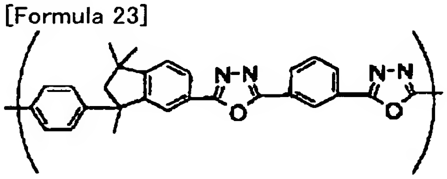
	ポリオキサジアゾール誘導体	1，1，2，2－テトラクロロエタン	クロロホルム	ジクロロメタン	NMP
実施例1	P1	○	○	○	○
実施例2	P2	○	×	○	○
実施例3	P3	○	○	○	○
実施例4	P4	○	×	△	△
実施例5	P5	○	○	○	○
実施例6	P6	○	○	×	○
実施例7	P7	○	×	△	△
実施例8	P8	○	○	△	○
実施例9	P9	○	○	○	○
比較例1	P10	×	×	×	×
比較例2	P11	×	×	×	×

[0102] (An example 2 - an example 9, and the example 1 of a comparison - the example 2 of a comparison) (Manufacture of a polyoxadiazole derivative) the raw material shown in Table 1 in examples 2-9 -- as a dicarboxylic acid component and a dihydrazide component -- using it -- the same conditions as an example 1, and a procedure -- with, the polyoxadiazole derivative (P2-P9) shown in following chemical formula (8) - (15) was manufactured. Moreover, also in the examples 1-2 of a comparison, the raw material shown in Table 1 was used, and the polyoxadiazole derivative (P10-P11) which are the same conditions and a procedure like an example 1, with is shown in chemical formula (16) - (17) was manufactured. In addition, each of a gram (g) unit and a millimol (mmol) unit has shown among the table the amount of the raw material used shown in Table 1.
[0103]
[Formula 22]



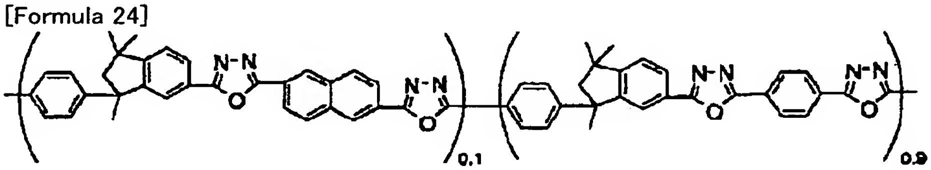
(8)

[0104]
[Formula 23]



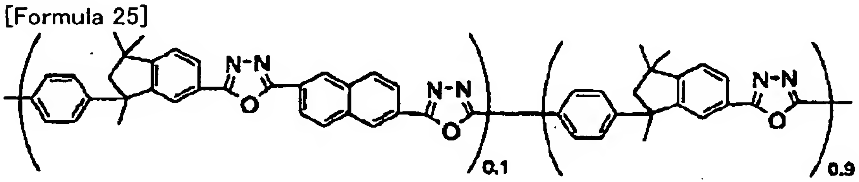
(9)

[0105]
[Formula 24]



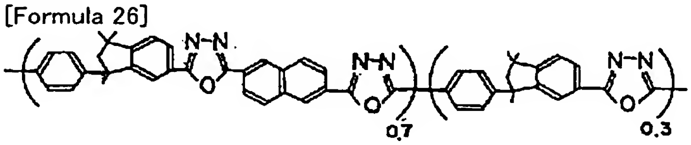
(10)

[0106]
[Formula 25]



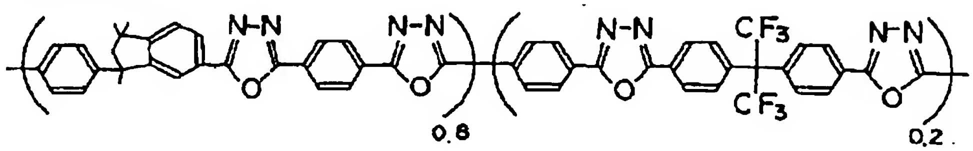
(11)

[0107]
[Formula 26]



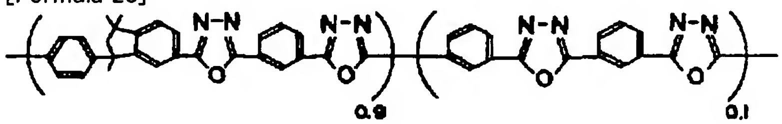
(12)

[0108]
[Formula 27]



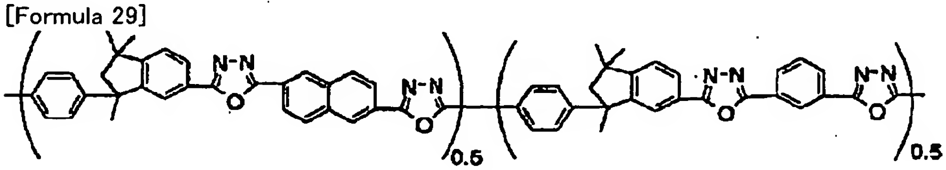
(1 3)

[0109]
[Formula 28]



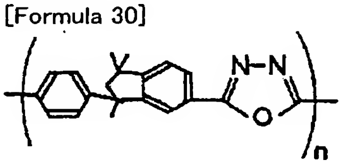
(14)

[0110]
[Formula 29]



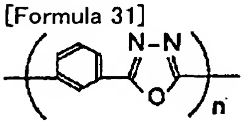
(1 5)

[0111]
[Formula 30]



(1 6)

[0112]
[Formula 31]



(1 7)

[0113] subsequently — the obtained polyoxadiazole derivative (P2-P11) — respectively — an example 1 — the same — carrying out — a logarithm — viscosity, glass transition temperature, and the decrease pyrolysis temperature of 5% weight were measured. A measurement result is shown in Table 2. In addition, since the obtained polyoxadiazole derivative was crystallizing only the example 2 of a comparison, glass transition temperature was not measured but the melting point was measured instead. Therefore, about the example 2 of a comparison, the value (*400 degree C) of the melting point is shown in the column of Tg among Table 2. Moreover, infrared spectroscopy measurement was performed like the example 1, respectively only about the polyoxadiazole derivative (P2-P9) obtained in the example 2 - the example 9. The chart of the obtained IR spectrum is shown in drawing 2 - drawing 9 , respectively.
[0114] Moreover, about the obtained polyoxadiazole derivative (P2-P11), like the example 1, the fluorescence spectrum (peak wavelength) was measured and the wavelength in the case of emitting light as an organic electroluminescent element was presumed, respectively. Furthermore, about the polyoxadiazole derivative (P10-P11) obtained in the examples 1-2 of a comparison, trifluoroacetic acid was used instead of 1, 1, 2, 2, and -tetrachloroethane, and the fluorescence spectrum (peak wavelength) was measured. The result obtained, respectively is shown in Table 2.
[0115] Moreover, the dissolution sex test to various solvents was performed like the example 1 about the obtained polyoxadiazole derivative (P2-P11), respectively. A result is shown in Table 3.
[0116] (Example 10)
(Creation of an organic electroluminescent element) On the glass substrate with a thickness of 1mm, it is 50nm in thickness, with the indium-tin-oxide compound (ITO) film was formed with the vacuum deposition method. moreover, this ITO film top — the Pori (p-phenylenevinylene) film of 50nm thickness — J.Appl.Polym, Sci., and Vol. — it formed in 26 and 3241 (1988) as an electron hole (hole) transportation layer by the approach of a publication.
[0117] Subsequently, rotation spreading of the solution (10 % of the weight of concentration) made to dissolve the poly oxazole derivative (P2) obtained in the example 2 in 1,1,2,2-tetrachloroethane was carried out on the Pori (p-phenylenevinylene) film using the spin coater. And at the temperature of 80 degrees C, it heat-treated for 2 hours and the poly oxazole derivative film of 50nm thickness was formed as an electronic transportation layer.
[0118] Subsequently, on the obtained poly oxazole derivative film, the vacuum deposition method was used, the

aluminum layer with a thickness of 100nm was formed as cathode in an organic electroluminescent element, and the organic electroluminescent element of this invention was created.
[0119] (Evaluation of an organic electroluminescent element) When the electrical potential difference of 28V was impressed between the ITO electrode of the organic electroluminescent element obtained by doing in this way, and the aluminum electrode, skillful green luminescence was observed. And when measured about the brightness of the luminescence concerned using brightness meter, it is 243 cd/m2. The value to say was acquired.
[0120]
[Effect of the Invention] Common organic solvents, such as 1,1,2,2-tetrachloroethane, can be provided now with a meltable polyoxadiazole derivative by including the OKISA diazole segment which has a phenyl indan radical in intramolecular.
[0121] Moreover, aromatic series dicarboxylic acid dihydrazide, and 1, 1, a 3-trimethyl-3-phenyl indan - 4' and by making 5-dicarboxylic acid react Or aromatic series dicarboxylic acid, and 1, 1, a 3-trimethyl-3-phenyl indan - 4' and by making 5-dicarboxylic acid dihydrazide react The polyoxadiazole derivative containing the OKISA diazole segment which has a phenyl indan radical as it is also at high recovery can be manufactured now.
[0122] Moreover, by using a meltable polyoxadiazole derivative for these common organic solvents, solution spreading was attained and manufacture of an organic electroluminescent element became easy. Furthermore, by solution spreading, since a uniform thin film formed easily, the organic electroluminescent element which was excellent in endurance with high brightness could be offered.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the organic electroluminescent element which used the polyoxadiazole derivative concerned for a polyoxadiazole derivative and its manufacture approach, and a list. It is related with the organic electroluminescent element using the still more nearly meltable polyoxadiazole derivative to the organic solvent concerned about a polyoxadiazole derivative meltable to a more detailed common organic solvent, and its manufacture approach.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved] In order to solve the above-mentioned problem, it has the outstanding electronic transport capacity, and it is meltable to an organic solvent, thin-film-izing is easy, and, moreover, development of a high molecular compound with high thermal stability with high glass transition temperature and pyrolysis temperature has been a technical problem. Then, a header and this invention are completed for having the electronic transport capacity which the artificers of this invention became meltable [polyoxadiazole] to an organic solvent by introducing into intramolecular the OKISA diazole segment which has a phenyl indan radical in a specific joint format as a result of inquiring wholeheartedly, and whose thermal stability was [the polyoxadiazole concerned] high and was moreover excellent.

[Translation done.]

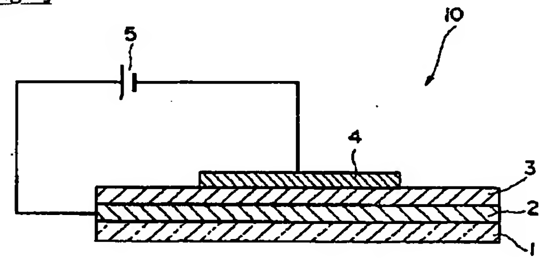
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the sectional view of the organic electroluminescent element in the operation gestalt of this invention.
[Drawing 2] It is drawing showing IR chart about the polyoxadiazole derivative in an example 1.
[Drawing 3] It is drawing showing IR chart about the polyoxadiazole derivative in an example 2.
[Drawing 4] It is drawing showing IR chart about the polyoxadiazole derivative in an example 3.
[Drawing 5] It is drawing showing IR chart about the polyoxadiazole derivative in an example 4.
[Drawing 6] It is drawing showing IR chart about the polyoxadiazole derivative in an example 5.
[Drawing 7] It is drawing showing IR chart about the polyoxadiazole derivative in an example 6.
[Drawing 8] It is drawing showing IR chart about the polyoxadiazole derivative in an example 7.
[Drawing 9] It is drawing showing IR chart about the polyoxadiazole derivative in an example 8.
[Drawing 10] It is drawing showing IR chart about the polyoxadiazole derivative in an example 9.
[Description of Notations]
1 Glass Substrate
2 ITO Film (Anode Plate)
3 Luminous Layer
4 Aluminum Layer (Cathode)
5 DC Power Supply
10 Organic Electroluminescent Element

[Translation done.]

DRAWINGS

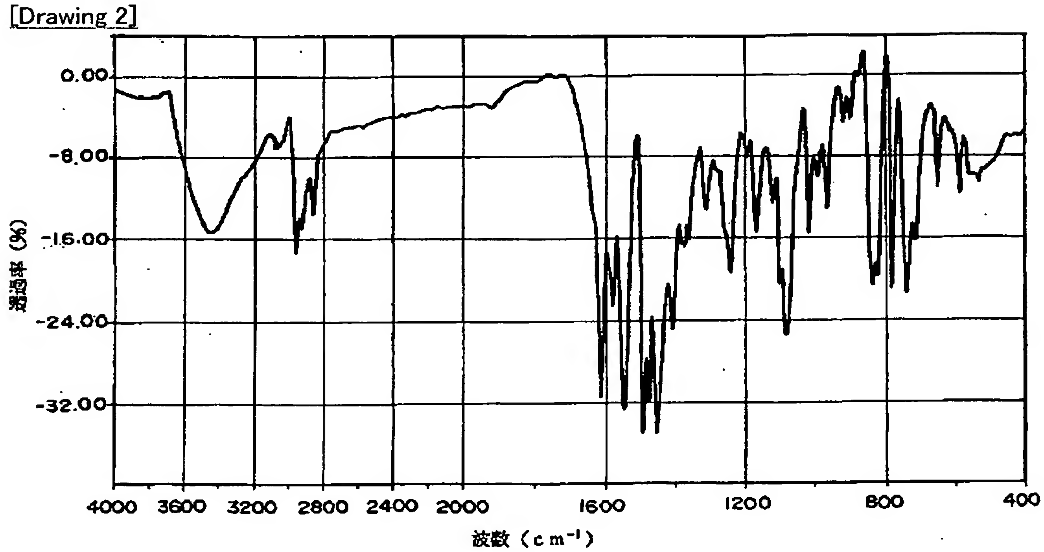
[Drawing 1]



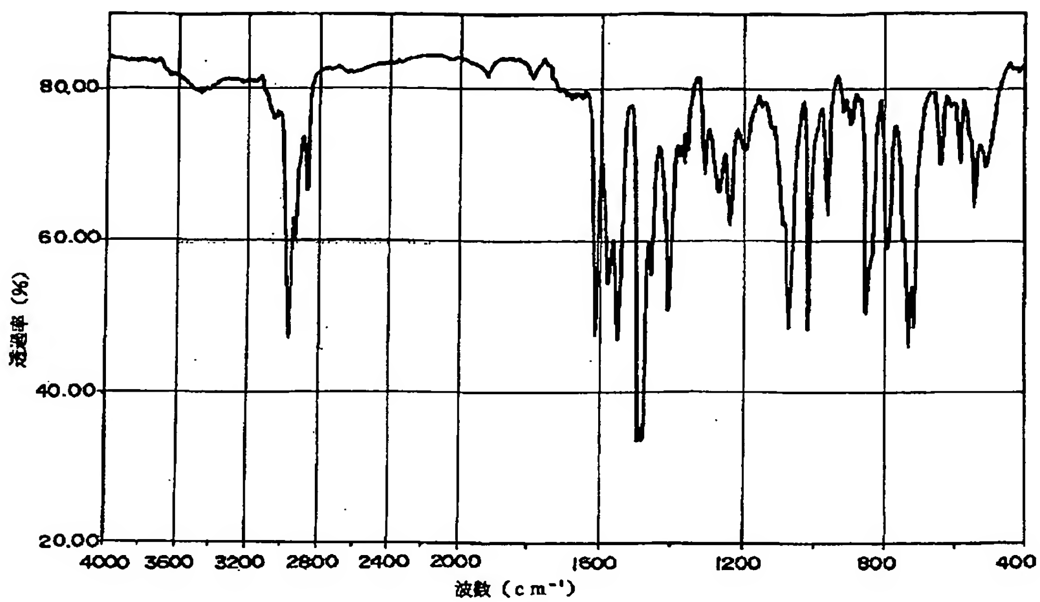
1. ガラス基板
2. ＩＴＯ膜（陽極）
3. 発光層
4. アルミニウム層（陰極）
5. 直流電源

10. 有機エレクトロルミネッセンス素子

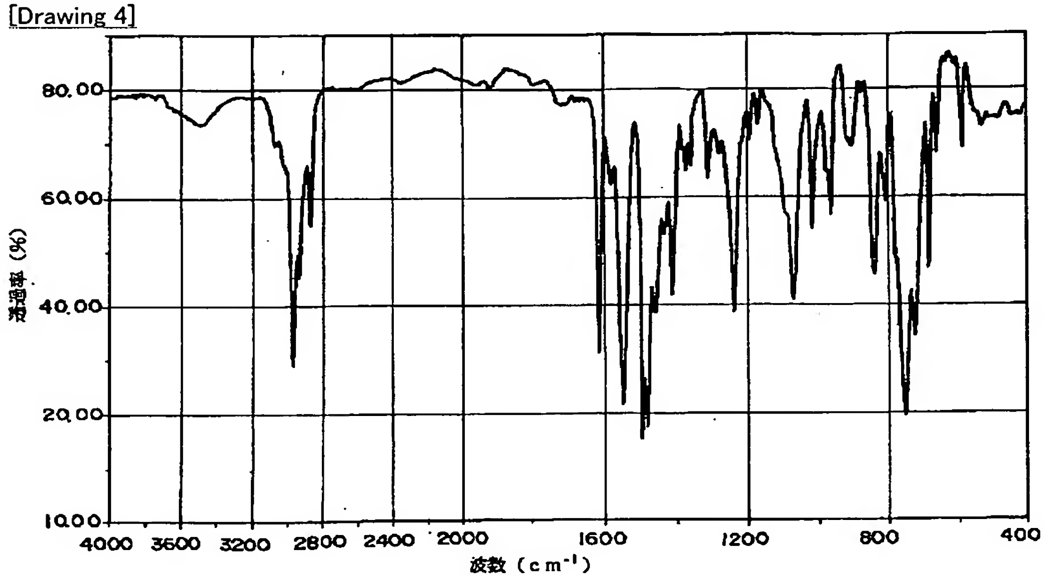
[Drawing 2]



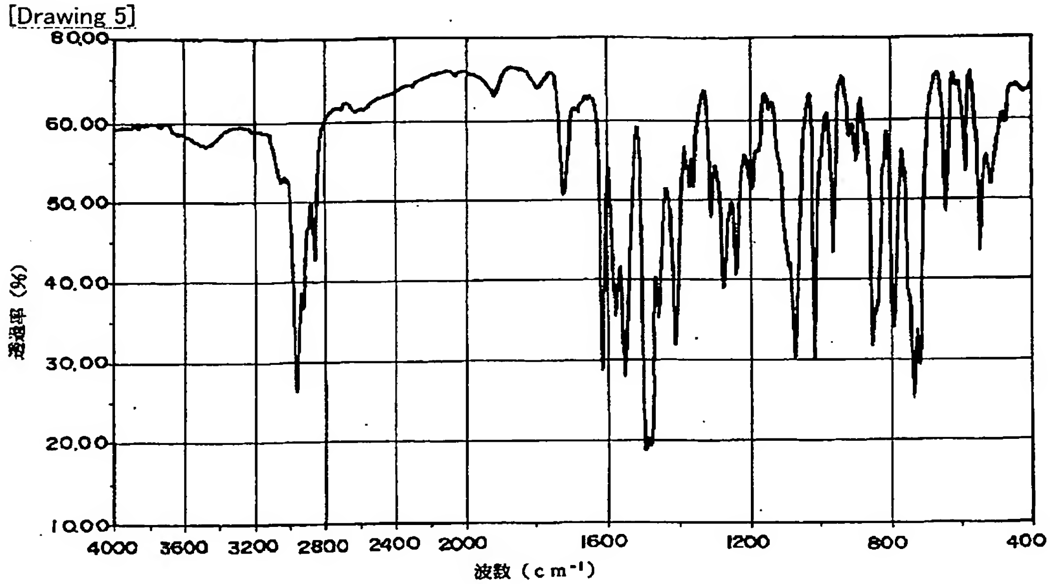
[Drawing 3]



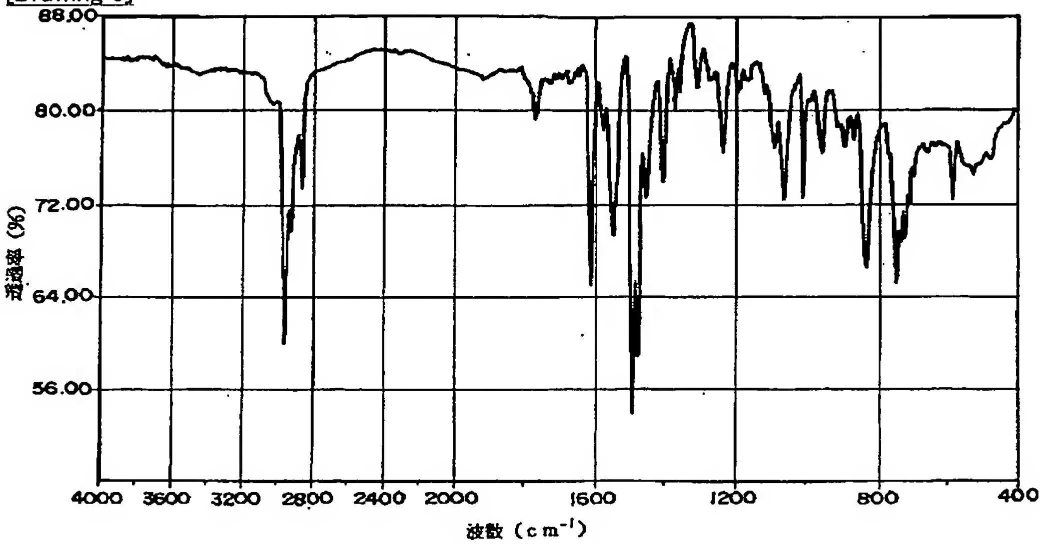
[Drawing 4]



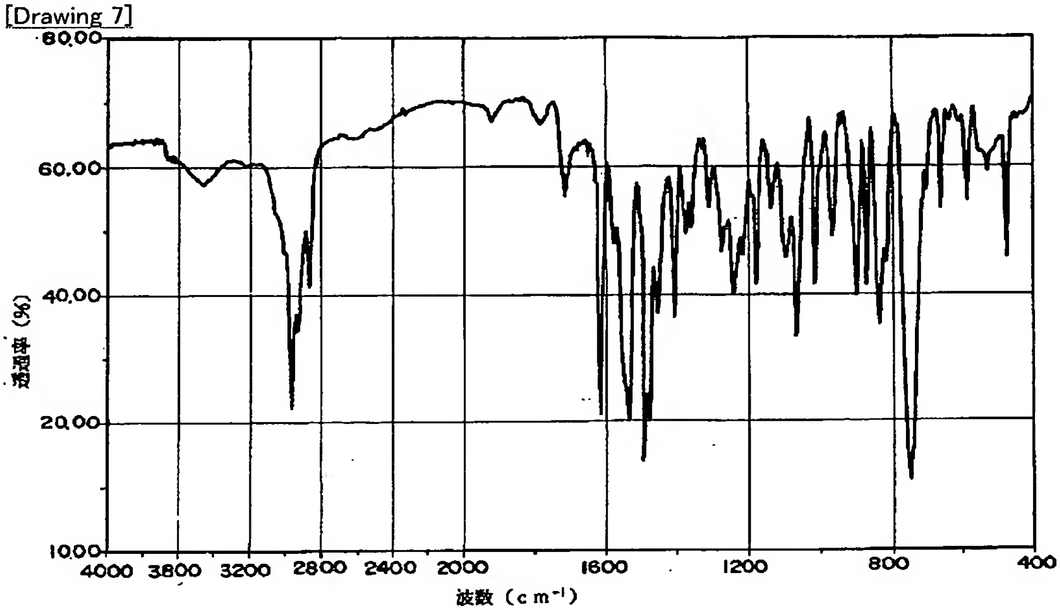
[Drawing 5]



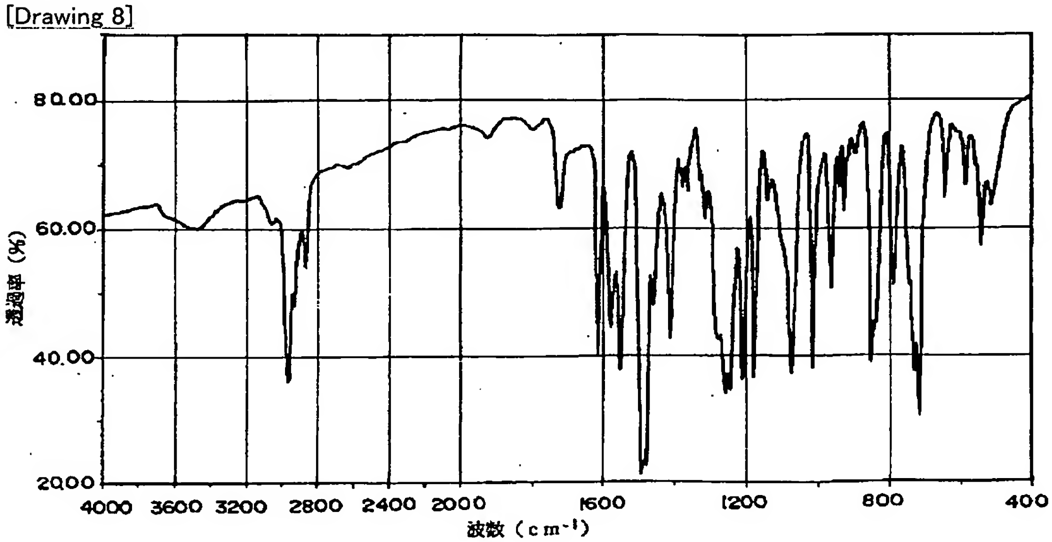
[Drawing 6]



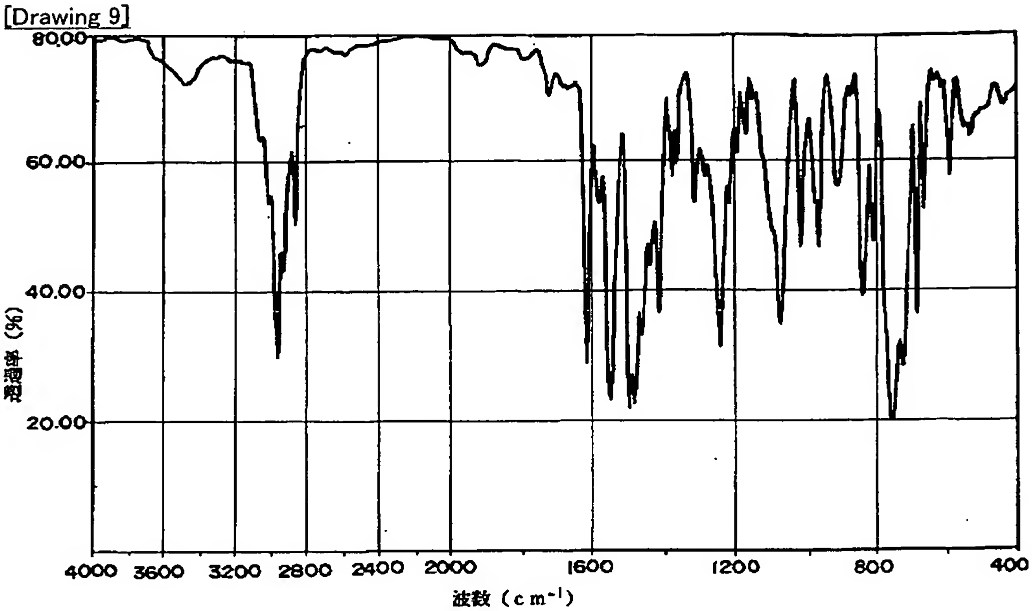
[Drawing 7]



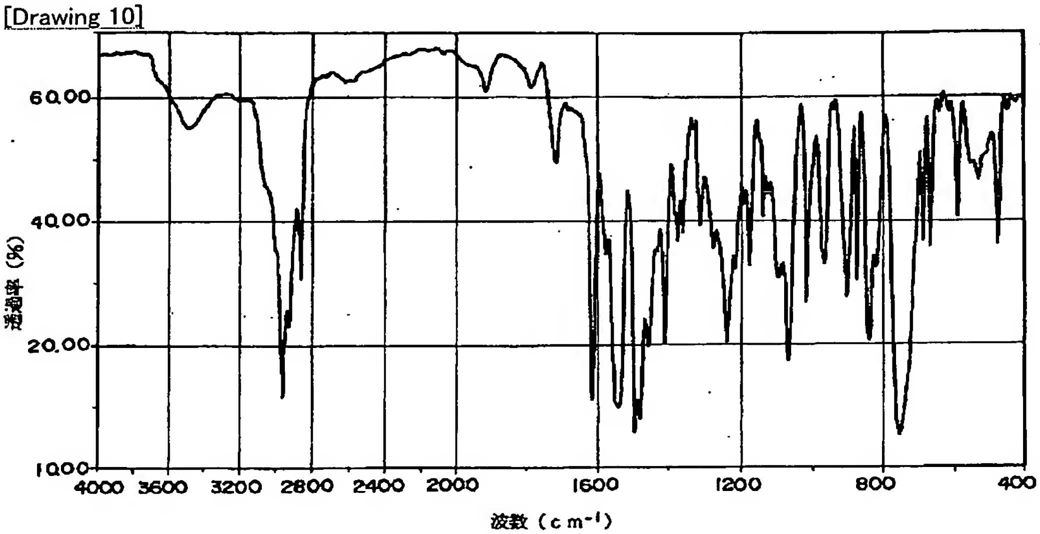
[Drawing 8]



[Drawing 9]



[Drawing 10]



[Translation done.]